THERMODYNAMIC PROPERTIES OF GASES

A thesis presented for the degree of

Doctor of Philosophy in Chemical Engineering

in the

University of Canterbury,

Christchurch, New Zealand

by

C.M. Couldwell

1975

ACKNOWLEDGMENTS

I wish to thank Professor A.G. Williamson for being an interested and interesting supervisor during the course of this work. Also, thanks are due to Dr P.J. McElroy who has offered his help and supervision to this project in general and especially while Professor Williamson was on leave.

I am indebted to the technical staff of the Department of Chemical Engineering who have cheerfully built and altered the experimental apparatus. The glass-blowing expertise of Mr F. Downing of the Chemistry Department, University of Canterbury, is very much appreciated. The assistance given by the cryogenic technicians of the Physics Department is also acknowledged.

I would also like to thank the University Grants Committee for financial assistance in the form of a Postgraduate Research Scholarship.

I wish to thank Mrs G.D. Niven for typing this thesis.

Enthalpies with knobbly knees
Were chasing Gibbs Free Energies,
Through lowered freezing points and more
Like cubed square roots of 84.

While coefficients large and small,
Fugacity and virial,
Were playing very hard to get
Since oil had got the gear all wet.

CONTENTS

1. SUMMARY

A new method for experimentally determining second virial coefficients of condensable gases is described.

This method avoids the difficult volume calibrations necessary with former techniques and evaluates the second virial coefficient in terms of three pressure measurements.

Measurements are reported for n-hexane at temperatures of 328.15 K, 343.15 K, 358.15 K and 373.15 K using this method.

These values do not agree with the generally accepted second virial coefficients from the literature and reasons are advanced to explain this.

2. INTRODUCTION

In chemical engineering, there is a need to understand p-V-T-x properties of gases for design purposes.

These properties have been the subject of study since the classical work of Robert Boyle in 1662. Other major advances over the intervening period have been the results of work by Jacques Charles who proposed (in 1802) a gas law where the pressure remained constant, John Dalton (1801) who gave his name to the law of additivity of partial pressures, Amadeo Avagadro (1811) who postulated that equal volumes of all gases contain equal numbers of molecules under the same conditions of temperature and pressure, and Amagat from whom, in 1880, we have a law of additive volumes. These laws can all be expressed by the equation generally known as the ideal gas law:

$$pV = \Sigma_i n_i \, RT \qquad (2.1)$$

where p is the pressure,

V is the volume,

$\Sigma_i n_i$ is the number of moles of the gas present, independent of the type,

R is the gas constant,

and T is the absolute temperature.

These laws are valid at low pressures, becoming exact as the limit to real behaviour as density tends to zero. Hence they are called the "perfect gas" relations. It is also interesting to note that the perfect gas relations may be derived from molecular considerations in a number of ways. For example, Hill (1962) uses statistical mechanics to derive the perfect gas law while Hirschfelder, Curtis and Bird (1954) use a detailed kinetic theory of gases.

At higher temperatures and pressures, real gases show significant deviations from perfect behaviour which depend on temperature, pressure and composition. An understanding of real gas behaviour is necessary in a large number of engineering applications since pressures of up to many thousands of bars are not uncommon. Much recent work has been devoted to

(a) equations of state suitable for imperfect gases,

(b) correlation of properties between different gases, and

(c) relations between the properties of mixed gases and those of the pure components.

Equations of state for imperfect gases:

The classical two-parameter equation of state is that of van der Waals who, in 1873, proposed the first practical equation to improve on the ideal gas law. Among the numerous other two-parameter equations of state are those of Dieterici, Berthelot and Redlich-Kwong:

van der Waals (1873) $$p = \frac{RT}{v - b} - \frac{a}{v^2} \qquad (2.2)$$

Dieterici (1899) $$p = \frac{RT}{v - b} e^{-a/vRT} \qquad (2.3)$$

Berthelot (1907) $$p = \frac{RT}{v - b} - \frac{a}{Tv^2} \qquad (2.4)$$

Redlich-Kwong (1949) $$p = \frac{RT}{v - b} - \frac{a}{T^{\frac{1}{2}}v(v+b)} \qquad (2.5)$$

where a and b are constants.

Unfortunately these only apply over a limited density and temperature range but are useful because of their simple form involving only two constants. Although these are simple equations, the graphical method employing the corresponding states principle is often used. In this procedure the compressibility factor, z, defined by the relation:

$$z = \frac{pv}{RT} \qquad (2.6)$$

is plotted versus reduced pressure, p_r, for lines of given reduced temperature, T_r. This method is convenient for practical purposes in that one chart can represent all gases.

There are a number of more cumbersome equations of state available which have more than two constants and which, by virtue of the fact that they have more constants, are more accurate in the regions of higher density where the simpler equations are not so accurate. An extreme example of this type of relation is the Benedict-Webb-Rubin equation (1940)

of state:

$$p = RT\rho + (B_oRT - A_o - \frac{C_o}{T^2})\rho^2 + (bRT-a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^3}{T^2}(1+\gamma\rho^2)e^{-\gamma\rho^2} \quad (2.7)$$

where $\rho = \frac{1}{v}$, and A_o, B_o, C_o, a, b, c, γ and α are eight constants which are determined empirically for each substance.

In 1901 Kamerlingh Onnes suggested the polynomial:

$$pv = A + \frac{B"}{v^8} + \frac{C"}{v^2} + \frac{D"}{v^4} + \frac{E"}{v^6} + \frac{F"}{v^8} \quad (2.8)$$

to fit p-V-T data. He called the "constants" A to F" "virial coefficients". The virial equation of state expresses the product of pressure and volume in a power series of 1/v. A similar power series in p is also used. The two forms of the equation are:

(1) the density series (or Leiden form)

$$pv = RT(1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \ldots) \quad (2.9)$$

where B(T) and C(T) are the second and third virial coefficients respectively for the density series, and

(2) the pressure series (or Berlin form)

$$pv = RT(1 + B'(T)p + C'(T)p^2 + \ldots) \quad (2.10)$$

where B'(T) and C'(T) are the second and third virial coefficients respectively for the pressure series.

The relations between the constants B,C,D,... and B',C',D',... can be obtained by inverting one equation of state into the other and equating coefficients. For example:

$$B(T) = B'(T) \quad (2.11)$$

$$C(T) = (B(T))^2 + C'(T)RT \quad (2.12)$$

The principle of corresponding states describes the dependence of the second virial coefficient on the temperature as:

$$B/V_c = \phi(T/T_c) \quad (2.13)$$

where V_c and T_c are the critical volume and critical temperature respectively. A requirement of this principle is that the molecules

must have spherical symmetry. McGlashan and Potter (1962) have fitted the second virial coefficients of argon, krypton, xenon and methane to the principle. Since all of these molecules have spherical symmetry, good agreement is expected and obtained, especially at temperatures greater than the critical. They then determined the deviations from the principle of corresponding states for the n-alkanes with the deviations bearing a relation to the chain length and the reduced temperature. This adds another parameter to the principle of corresponding states and for the n-alkanes the virial coefficient is given by:

$$B/V_c = 0.430-0.881(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \qquad (2.14)$$

where n is the chain length.

Statistical mechanics indicate that the contribution of the second, third, fourth, ... virial coefficients represent the deviations from ideal behaviour when interactions involving two, three, four, ... molecules become important in the gas.

Second virial coefficients can be used in a variety of ways to provide further properties of gases. Hirschfelder, Curtis and Bird (1954) have summarised the deviations of some thermodynamic functions from the ideal values in terms of virial coefficients.

If the pressure series virial equation is truncated at the term in the third virial coefficient:

$$pv = RT(1 + B'p + C'p^2) \qquad (2.15)$$

and from p-V-T data a graph of pV versus p is plotted, then the second virial coefficient can be obtained as the slope of the line. The third virial coefficient is then the curvature of the line.

Since many of the gases encountered industrially are gas mixtures, it would be convenient if their properties could be calculated from the properties of the pure components. The second virial coefficient of a two-component mixture is given by:

$$B_m = x_1^2 B_{11} + 2x_1x_2B_{12} + x_2^2 B_{22} \qquad (2.16)$$

where x_1 and x_2 are the mole fractions of each of the components of the mixture.

B_{11} and B_{22} are the pure component second virial coefficients resulting from interactions between like molecules, and

B_{12} is the crossed second virial coefficient resulting from interactions between unlike molecules. Hence the second virial coefficient for mixtures depends on forces between unlike molecules as well as the forces between molecules of the same species. Consequently, to obtain information about these unlike species interactions it is necessary to have accurate experimental data for both the pure components and the mixtures. It is the former only with which this thesis will be concerned.

3. REVIEW OF EXPERIMENTAL METHODS

3.1 Experimental Methods for the Determination of Virial Coefficients of Pure Gases

3.1.1 Classification of Methods

A very large number of the determinations of second virial coefficients depend on the measurement of pressure, volume, temperature and where necessary the number of moles of gas present. Experimental techniques fall into two fairly well-defined groups: those in which the gas is at high pressure and those where the gas pressure is low. Work in the low-pressure region usually uses methods where the pressure is measured with a mercury column, while the high pressure studies use mainly free piston gauges. In addition to these methods a wide range of methods have been applied which have used other techniques for measuring the density of the gas thus avoiding problems encountered with volume calibrations. In general, this latter group comprises methods which measure some property of the gas which depends on its non-ideality. The measurements for the low-pressure p-V-T methods (section 3.1.3) and the high-pressure p-V-T methods (section 3.1.4) may be made directly on the gas under investigation or the behaviour may be compared with a reference gas under the same conditions.

Since the measurement of pressure, temperature and density are common to many of the methods, a brief summary of these will be given.

3.1.2 Measurement of Experimental Quantities

3.1.2.1 Moles of Gas

Many methods used to determine second virial coefficients assume that the number of moles of gas in the apparatus remains constant. However, the adsorption of some of the gaseous vapour on the walls of the apparatus can contribute an error in the calculation of the second virial coefficient.

In some experimental procedures, such as the Boyle method, the value of n, the number of moles of gas, is obtained by extrapolating a plot of

pV versus p to zero pressure. According to the truncated pressure series equation:

$$pV = n(RT + Bp) \qquad (3.1)$$

the intercept at zero pressure is nRT. The value of n obtained from this intercept is then used with the limiting slope, nB, to obtain the second virial coefficient. This method is the one used by Lambert, Roberts, Rowlinson and Wilkinson (1949) in their experiments with a number of organic vapours. It is usual with this procedure to consider that the third virial coefficient is zero so that a straight line drawn through the experimental points will have the same slope as the limiting slope. Whytlaw-Gray and Bottomley (1957) have attributed curvature in pV versus p isotherms at low pressures to the effect of adsorption. Since, at these low pressures, the effect of a third virial coefficient is unlikely to be as great as that apparently observed, they felt that the adsorption of some of the sample gas on the walls of the apparatus was the cause of this curvature. When both the apparatus walls and mercury in contact with these walls and the test gas were scrupulously clean, then this effect was minimised. Eubank and Kerns (1973) have suggested that the effects of adsorption can be seen in a Burnett apparatus calculation as indicated by an apparent shift of the apparatus constant. Careful preparation of the apparatus surfaces to reduce the surface area and to present a clean surface to the sample gas are mentioned as being ways of reducing this effect. The more polar the gas the greater will be the amount of adsorption. For the gas density balance constructed by Haworth and Sutton (1970) a plate was fused to the opposite side of the beam to the float in an attempt to nullify the effects of adsorption. The adsorption effects become greater as the gaseous sample becomes more dense so that near the saturated vapour pressure this adsorption effect is a very real problem. In the indirect methods of determining second virial coefficients the results are not complicated by the effects of adsorption.

A typical physical adsorption isotherm is shown in figure 3.1.

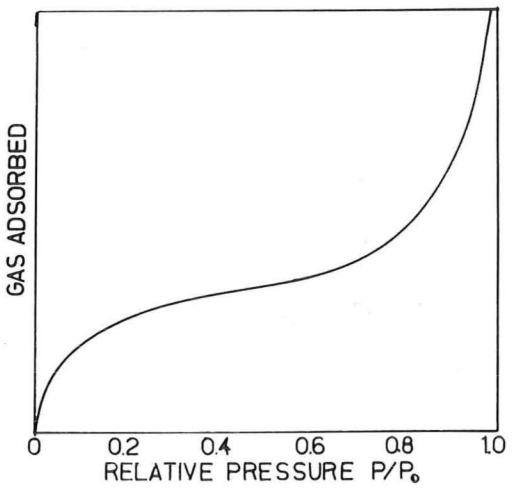


FIGURE 3.1 - ADSORPTION ISOTHERM

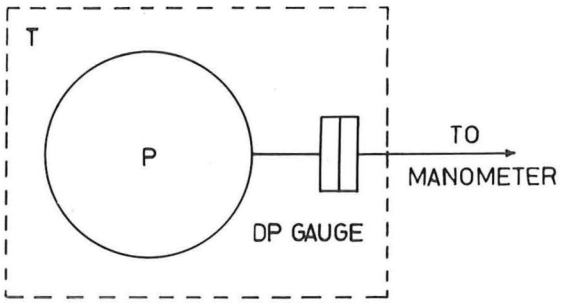


FIGURE 3.2 - NULL PRESSURE INDICATOR

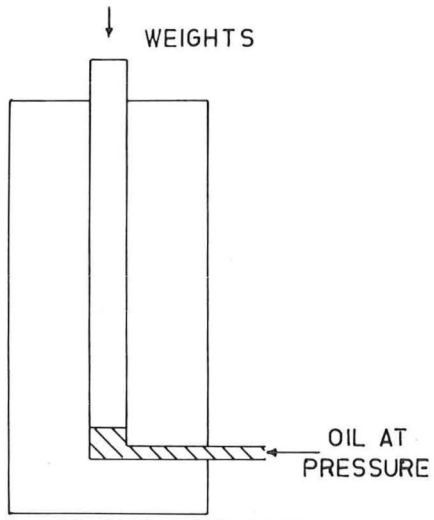


FIGURE 3.3 - SIMPLE FREE-PISTON GAUGE

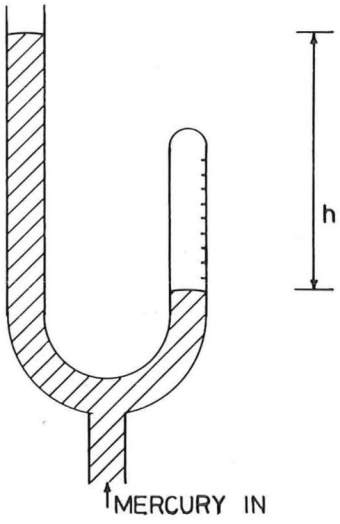


FIGURE 3.4 - BOYLE'S LAW APPARATUS

FIGURE 3.5 - HIGH PRESSURE BOYLE'S LAW APPARATUS

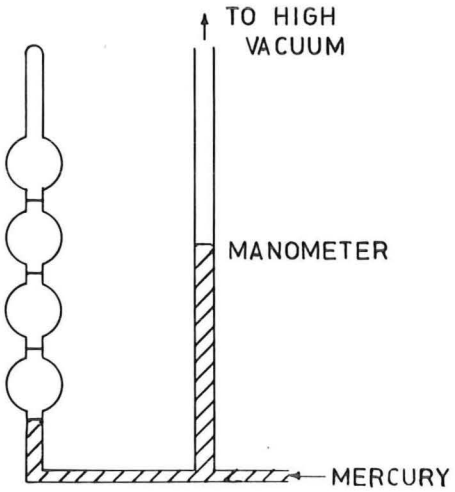


FIGURE 3.6 - FIXED-VOLUME BOYLE APPARATUS

If the apparatus is being used in the initial steep or curved portion of the curve or the latter parts, then the effects of adsorption are much more severe than if the apparatus were being operated in the middle 'flat' portion. Although working in this middle section of the isotherm does not avoid the adsorption problem completely, it certainly reduces it. Bottomley, Reeves and Whytlaw-Gray (1958) have given some figures for the adsorption of benzene vapour on pyrex glass at various pressures. These values are in the range of 200 parts per million of the total vapour phase adsorbed. After the results were corrected for the adsorption effect the value of the calculated second virial coefficient changed by 20×10^{-6} $m^3\ mole^{-1}$.

3.1.2.2 Pressure Measurement

Pressure measurements can be divided into two basic sections: those at low pressures or up to a few bars and those at pressures greater than this.

Low pressures are for the most part measured by mercury manometers. When using small-bore manometers (less than 1 to 2 cm diameter tubing), the capillary effect must be taken into account. The value of the pressure as given by the formula, $p = \rho gh$, requires that the local acceleration because of gravity, g, be known accurately. This is not usually difficult to obtain. The density of mercury, ρ, must also be known to a high degree of accuracy. This is readily available as a function of temperature which then requires that the temperature of the manometer in use must also be known. Hence manometers are thermostatted. The heights of each leg of a mercury manometer are usually measured with a precision cathetometer. The engraved bar of a cathetometer is accurate at a given temperature. Usually it is made of a material of low coefficient of thermal expansion so that if any correction is necessary to the bar height it is minimal. For this correction to be made, the temperature of the cathetometer must be known.

Where high pressures are to be measured with mercury manometers, it is possible to construct a manometer consisting of a number of mercury manometers in series. These multiple manometers have been used up to pressures of several hundred atmospheres but are inconvenient to use. Temperature control is a problem when there are many mercury heights to be read for what amounts to one pressure reading.

The problem of mercury dissolving some of the sample gas, which occurs at higher pressures, as well as the gas becoming a binary mixture with mercury as one component, can be overcome by placing a differential pressure transducer in the apparatus to be used as a null indicator as shown in figure 3.2. One side of the transducer is in contact with the gas under investigation while the other side is in contact with another gas, such as nitrogen, which is also in contact with one side of a mercury manometer. This type of arrangement also avoids the problems associated with having the mercury manometer at the same temperature as the experimental apparatus. The Boyle apparatus of Alexander and Lambert (1941) is one in which the pressure measuring device is at the temperature of the experiment.

At high pressures the most common measuring device is the free-piston gauge. The gas at pressure p exerts this pressure on a fluid (usually oil) which in turn acts on a piston inside a cylinder. The oil tends to push the piston out of the cylinder but is opposed by weights which are applied to it as shown in figure 3.3. At very high pressures this opposing force may be applied by stiff springs. A review by Bridgman (1949) gives examples of the various types of free-piston gauges. In particular cases gauges were developed to overcome one or more of the three sources of error in free-piston gauges. These errors are: (1) friction, (2) leaking of the pressure transmitting fluid through the annulus between the piston and cylinder, and (3) distortion of the gauge which changes the effective area of the gauge. One advantage that the free-piston gauge has overother pressure gauges is that the weight on

the piston automatically fixes the pressure of the system. Deadweight piston or free-piston gauges have been used to measure pressures of up to 6 k bar with a precision of ±0.05%. Deadweight gauges that operate pneumatically are now becoming available. These not only operate in the high-pressure region up to a few hundred bars but also at low pressures. At low pressures, up to one bar, they can have an accuracy of less than 1 N m^{-2} which compares very favourably with mercury manometers.

Although mercury manometers and free-piston gauges are the most commonly used pressure measuring devices there are other types in use.

In a bourdon tube gauge the tube is displaced by the pressure difference between the pressure applied to the tube and that surrounding the tube. Under pressure the oval-shaped (usually) tube tends to become circular. The free end of the tube is attached to a pointer to give an indication of the pressure. Ulmer (1971) states that these devices are used at pressures of up to 6 kb with a precision of 0.1%. Part of the lack of precision comes from the fact that they are usually calibrated against deadweight gauges which in themselves have some inaccuracies.

Quartz bourdon gauges can be used at pressures of up to about 5 bars with an accuracy of up to 150 N m^{-2}. These incorporate a fused quartz spiral in place of the usual bourdon tube. Another type of quartz bourdon tube measures pressure by the amount of electrical current that it is necessary to apply to electromagnetic coils to oppose and exactly balance the rotation of the tube.

The marganin pressure gauge operates on the principle of the changing resistance of a wire when subjected to pressure. Marganin is an alloy of copper (80 to 84%), manganese, nickel and iron. Since the resistance of metals also changes with temperature they can only be used with devices that operate at constant temperature. The pressure coefficient of resistivity is about 1.1 x 10^{-6} per bar and is linear over a wide pressure range. Hence they need only one fixed point for the calibration.

The precision of these devices also depends on that of the deadweight tester against which they are usually calibrated.

A number of types of pressure transducers have been developed which rely on changes in electrical or magnetic properties with pressure. One type has a metal diaphragm that acts as one plate of a capacitor. As the pressure is applied the diaphragm moves with respect to a fixed plate to change the thickness of the dielectric between the plates. With a suitable bridge circuit, the variation in capacitance can be measured and calibrated against pressure. Another transducer using a movable magnetic diaphragm is that of the variable reluctance type. The magnetic vane is positioned between two magnetic output coils such that any displacement of the diaphragm caused by the applied pressure changes the inductance ratio between the two coils. This voltage output can be calibrated against pressure.

Quartz crystals can be used as pressure transducers. The crystal oscillates at a given frequency provided that the pressure remains constant. In the sensorprobe of a quartz crystal pressure-measuring device, there is also a reference oscillator whose resonant frequency is independent of pressure. The difference between the quartz crystal oscillator frequency and that of the reference oscillator is used as a measure of the pressure applied to the crystal. These devices can have a precision of $\pm 10^3$ N m^{-2} over a pressure range as wide as 0 to 800 bars.

The SI unit of pressure is the Newton per square metre, N m^{-2}, which is also called the Pascal and denoted by the symbol Pa. Since the Pascal is too small for convenience it is often replaced by the bar, which is equal to 10^5 Pa, in reporting p-V-T data. The standard atmosphere has now been defined as 1.01325 bar exactly.

3.1.2.3 Temperature Measurement

The most readily available means of measuring temperature is the liquid in glass thermometer. These are capable of reading to a few tenths of a degree or, in the case of more sophisticated thermometers, to a few thousandths of a degree. The Beckmann thermometer is used for measuring temperature differences.

Thermocouples primarily measure a temperature difference - the difference between that of the cold and hot junctions. The reference junction may be held at any convenient temperature but it is usual to keep it at the ice point. Thermocouples of one sort or another cover a wide range of temperatures but are only capable of measuring temperatures to $\pm 0.01^{o}C$.

Although thermocouples determine temperature differences, the platinum resistance thermometer determines temperature ratios. This ratio is that of a resistance at a given temperature and that of the standard resistance which is thermostatted. These are the most accurate temperature measuring devices while the international temperature scale is defined within the temperature range of -182.97 to $630.5^{o}C$ by these thermometers.

The SI unit of thermodynamic temperature is the Kelvin, denoted by the symbol K. Since the Kelvin temperature scale is not an entirely practical scale to use, values on a more practical scale are often used. The Celsius temperature scale or International Practical Scale of Temperature is consequently used where one Kelvin degree is identical with one Celsius degree, while in absolute terms the Celsius temperature is defined as thermodynamic temperature less 273.15 K.

3.1.2.4 Volume Measurement

Although all experiments aiming at determining second virial coefficients involve direct measurements of temperature and pressure, it is with the measurement of volume or density that many of the experimental techniques vary.

The most direct method is to determine both the mass of gas and the

volume it occupies separately to obtain the density or molar volume. Some experiments determine density by refractive index or nuclear magnetic resonance techniques while others such as the Burnett method and other expansion methods avoid a direct density determination. At high pressures the mass of gas may be determined by direct weighing or by expanding the gas to a low pressure where the volume is measured. This requires that the equation of state be known at the low pressure to which the gas is expanded and is called the 'normal volume' technique. A technique used quite commonly for determining volumes is to fill the apparatus with a fluid of known density. The mass of this fluid contained within the unknown volume is then used to determine the volume. When using fluids with high densities, such as mercury, or fluids at vastly different densities than those to be tested, thought must be given to the possibility of the volume changing slightly during the volume determination.

The SI unit of volume is the cubic metre, m^3, and the SI unit of density is the kgm^{-3}. Although it is used very infrequently now, the historical unit of volume for gas measurements is the Amagat unit. The Amagat volume of a gas is the ratio between its volume at any temperature and pressure and its volume at 273.15 K and at one atmosphere pressure for a given mass of gas.

3.1.2.5 Reference Gases

Experiments of a relative nature where the behaviour of the sample gas is compared with that of a reference gas under the same conditions are used to determine second virial coefficients. The reference gas is usually one that is more nearly ideal than the gas under investigation or one with well-known p-V-T properties in the region of the experiment. Relative methods have almost never been used at high pressures while at low pressures there are quite a number of techniques that embody some sort of relative measurement. These will be described in a later section.

The most commonly used reference gases are: helium, argon and the

much more freely available nitrogen, all of whose second and third virial coefficients are well known over a wide range of temperature.

3.1.3 Low Pressure p-V-T Experimental Methods

3.1.3.1 p-V-T-n Method

The Dumas method used for determining the molecular weight of gases in which the pressure, temperature and mass of a given volume of gas are measured can be extended to investigate second virial coefficients. This method used by Roper (1940) is an example of what the simple equation of state suggests. This involves measuring p, T, V and n, although strictly speaking it is the density, ρ, that is important rather than V and n. A container of known volume is loaded with a weighed amount of sample and the pressure of the gas is measured at a given temperature. Roper determined the amount of gas in his experimental globe by weighing it evacuated and filled, making use of an identical counterpoise to provide buoyancy and adsorption corrections. The Kamerlingh Onnes form of the equation of state:

$$pv = RT\left(1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots\right) \qquad (3.2)$$

truncated to the term in the second virial coefficient gives:

$$pv = RT + \frac{RTB}{v} \qquad (3.3)$$

to the extent that 3.3 is an accurate representation of the gas behaviour. The second virial coefficient, B, is then given in terms of the measured quantities p, V, T and m by:

$$B = \frac{pv^2}{RT} - v \qquad (3.4)$$

Since all of these quantities were measured for each loading of the apparatus, a value of the second virial coefficient at each temperature was found. Barton and Hsu (1969) used an apparatus similar to that of Roper for p-V-T-n measurements with formic and acetic acids. The volume of their cell was determined in a similar manner to that of Roper's - by weighing empty and full with distilled water. An aluminium diaphragm

between the sample and the mercury manometer, with which the pressures were measured, prevented contamination of the sample with mercury and avoided mercury vapour pressure problems at the higher temperatures. Eon, Pommier and Guiochon (1971) also used a similar apparatus but used a small mercury null manometer in the constant temperature bath between the sample and the external manometer. The results obtained by these researchers were used to calculate the pressure series second virial coefficient:

$$B' = \frac{RT}{p}(z - 1) \qquad (3.5)$$

where z, the compressibility factor, is given by:

$$z = \frac{pv}{RT} \qquad (3.6)$$

3.1.3.2 Boyle's Method

The first quantitative p-V-T measurements were carried out by Boyle in the seventeenth century. His apparatus, as shown in figure 3.4, consisted of two legs joined at the bottom where there was provision for the addition and removal of mercury. One leg was open while the other leg, which was calibrated to serve as a gas burette, was closed at the top and sealed at the bottom by mercury. Addition or removal of mercury allows the pressure and volume of the gas in the burette to be changed. Boyle's law states that for a given mass of gas at constant temperature the volume is inversely proportional to the pressure. Although the observations made by Boyle are only exact if the gas is behaving perfectly, the deviations of a real gas from perfect behaviour may be used to determine the second virial coefficient.

When the gas is compressed by mercury the vapour pressure of the mercury puts an upper limit on the temperature to which this type of apparatus, in its original form, may be used. Sometimes a differential pressure gauge is placed between the sample gas that has been compressed by the mercury column and the pressure measuring device. This has the advantage that the pressure measuring manometer does not need to be at

the same temperature as the compression apparatus and that of the sample gas. The nitrogen (usually) pressure which nulls the pressure transducer is measured on an external manometer.

A simple Boyle's Law apparatus as described by Alexander and Lambert (1941) and used by this group, as well as Lambert, Roberts, Rowlinson and Wilkinson (1949) and Lambert, Clarke, Duke, Hicks, Lawrence, Morris and Shone (1959) compresses the gas into a graduated tube using a mercury column. The pressure is read as the difference between the mercury heights in the two legs of the apparatus while the whole apparatus is held at a constant temperature in a thermostat. A variation on the simple Boyle apparatus, used by Cawood and Paterson (1932), is one in which the graduated tube was a projection on a much larger bulb as illustrated in figure 3.5. This method, however, is usually used at high pressures. A further extension of the Boyle apparatus is to have the sample gas compressed through a series of predetermined and accurately known volumes. When two fixed volumes are used, as by Andon, Cox, Herington and Martin (1957) and Cox and Andon (1958), it is only necessary to know the volume ratio rather than the exact volumes. This volume ratio is usually determined with a gas whose equation of state is well known. A similar form of this apparatus as described by Guye and Batuecas (1923) used three accurately calibrated bulbs. This idea can be extended to many bulbs to provide a step-wise compression. Hajjar, Kay and Leverett (1969) used an apparatus with four bulbs as shown in figure 3.6. The amount of the sample was found by confining the liquid to the calibrated tip with mercury. The liquid sample was vaporised and the pressure measured as it was compressed through the various bulbs. A similar apparatus devised by Knoebel and Edmister (1968) was used for mixtures as well as pure substances. As has already been mentioned, the Boyle type of experiment is limited by the vapour pressure of mercury when this is used as the compressing fluid. Cottrell and Hamilton (1956) have developed an apparatus (figure 3.7) where the gas under investigation is not in contact with mercury. Instead of being compressed by a rising

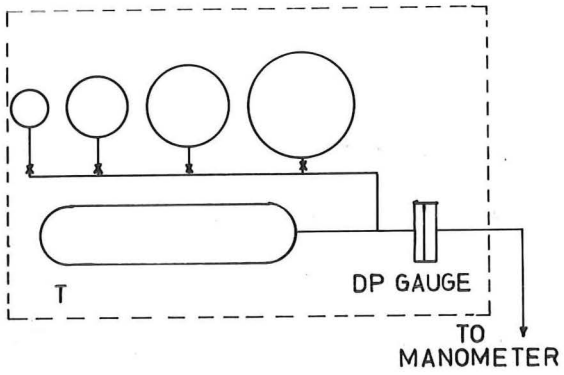


FIGURE 3.7 - MERCURY-FREE EXPANSION APPARATUS

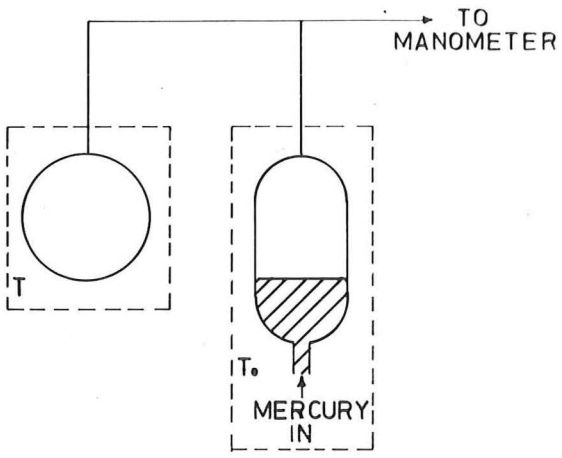


FIGURE 3.8 - CONSTANT-PRESSURE GAS THERMOMETER

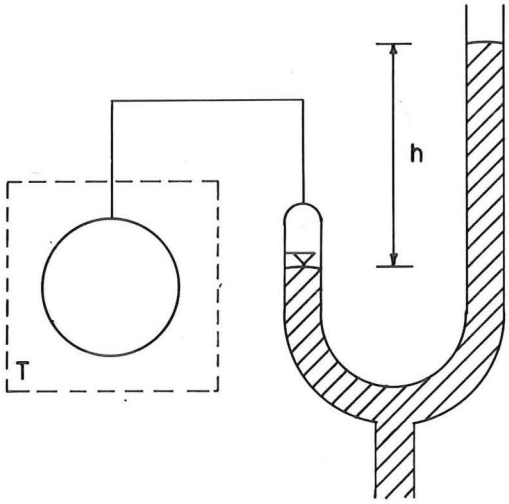


FIGURE 3.9 - CONSTANT-VOLUME GAS THERMOMETER

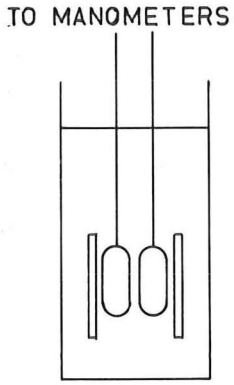


FIGURE 3.10 - LOW TEMPERATURE CONSTANT-VOLUME APPARATUS

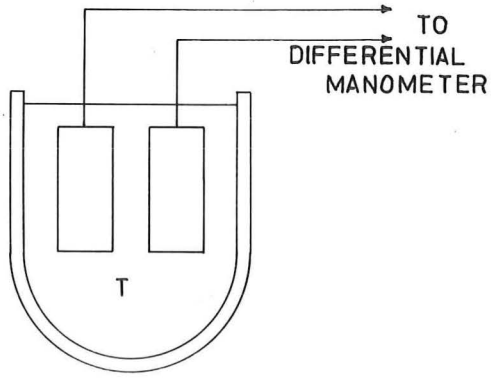


FIGURE 3.11 - DIFFERENTIAL PRESSURE APPARATUS

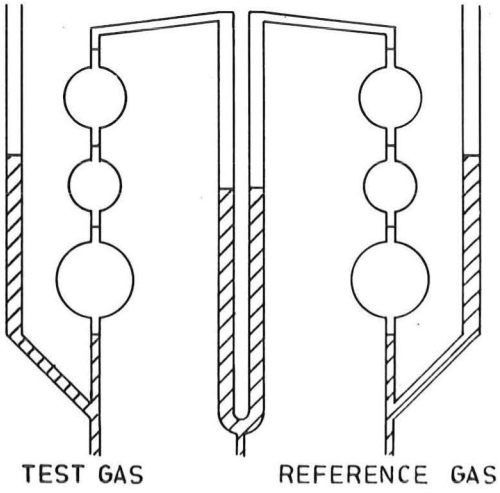


FIGURE 3.12 - DIFFERENTIAL COMPRESSION APPARATUS

mercury interface, the sample is expanded into a series of accurately known volumes and the pressures are determined by using a differential pressure transducer and an external manometer. The volumes of the various bulbs, tubing and transducer were determined by expanding nitrogen at its Boyle temperature.

The calculation of the second virial coefficient from the Boyle apparatus and its modifications is in most cases the same. From the pressure series virial equation:

$$pV = nRT + nB'p \qquad (3.7)$$

it can be seen that by plotting pV versus p the slope of the resulting straight line will be nB' and the y-axis intercept nRT. From the density series equation:

$$pV = nRT\left(1 + \frac{n}{V} B\right) \qquad (3.8)$$

a plot of pV versus $\frac{1}{V}$ has a slope of n^2BRT with a y-axis intercept of nRT.

3.1.3.3 Gas Thermometers

An apparatus in which both the amount of gas and either the volume or pressure are kept constant while the temperature changes is called a constant-volume or a constant-pressure gas thermometer. Although second virial coefficients have been measured with both constant-volume and constant-pressure gas thermometers in the past, they have not been so commonly used in recent times.

In a typical constant-pressure gas thermometer as used by Bartels and Eucken (1921) and shown in figure 3.8, there are two volumes filled with the sample gas. One, a fixed volume, is held in turn at the various temperatures at which the experiments are being done while the other is a variable volume, connected to the first with fine tubing and held at some fixed temperature (often $0^{\circ}C$). As the temperature of the fixed volume is changed the pressure is kept constant by injecting gas from the variable volume to the fixed volume or by removing gas from the variable volume to the fixed volume, usually with the aid of mercury. A series of runs is

carried out at differing constant pressures and the second virial coefficients calculated from the results after the amount in the constant volume has been determined. The amount of gas in the constant volume bulb is found by subtracting from the total, the amount in the variable volume. In order to determine this the equation of state for the gas must be known at the temperature at which the variable volume is kept. In the density series virial equation, all of the terms are known except the second virial coefficient. Hence at any of the temperatures at which the experiment was performed a value of B may be found; i.e.

$$B = \frac{V}{n}\left(\frac{pV}{nRT} - 1\right) \qquad (3.9)$$

Constant-volume gas thermometers are much more common than the constant-pressure gas thermometer. In this type of gas thermometer, the sample gas is loaded into the constant volume and confined there by one leg of the pressure measuring manometer, as shown in figure 3.9. The temperature of the gas sample is varied with the mercury level held fixed and the different pressure readings taken. As the temperature is varied the density should, ideally, stay constant but in actual fact it does not do so because of the dead spaces in the manometer and the connecting capillary which are not held at the same temperature as the constant volume. This technique has been used by White, Hu and Johnston (1953). The density of the gas under investigation may however be kept constant but this involves maintaining the manometer at the same temperature as the sample gas which then limits the range of temperatures over which this experiment may be performed. By using a null pressure indicator kept at the same temperature as the sample gas and an external manometer with nitrogen to balance the null pressure indicator, this problem can be overcome. Opel and Schaffenger (1969) used a fused quartz spoon gauge at temperatures up to 350^{o}C. Kistemaker and Keesom (1946) have suggested a type of double constant volume apparatus to reduce the low temperature problems of: (1) uncertainty in the pressure determination, (2) inability to maintain a constant temperature for a necessary length of time, and

(3) the amount of gas in dead spaces within the apparatus. This apparatus, shown in figure 3.10, involved two similar volumes, loaded to different gas densities, surrounded by a copper mantle. Two points on the pV isotherm were measured simultaneously at low pressures, these being sufficient to enable a second virial coefficient to be determined. The construction of the apparatus ensured that both volumes were at the same temperature thus avoiding the low temperature stability problem. The problems associated with the pressure determinations were overcome by using an X-ray shadowgraph method. The dead space problem was reduced by making such volumes as small as possible. With this method the second virial coefficient was determined from the density equation for each volume:

$$(pv)_1 = RT(1 + B\rho_1) \qquad (3.10)$$

and $$(pv)_2 = RT(1 + B\rho_2) \qquad (3.11)$$

Hence the difference equation:

$$\frac{(pv)_1 - (pv)_2}{(\rho_1 - \rho_2)} = RTB \qquad (3.12)$$

will provide a value of B. Keller (1955) also devised a constant volume experiment to avoid the difficulties encountered at low temperatures as mentioned above. Since Kistemaker and Keesom did their experiment in the late 1940's, there have been improvements in manometry and temperature control so that modern techniques have surmounted these problems. Keller managed to avoid the dead space difficulty by measuring the gas in these volumes after the completion of the experiment. Keller fitted his isotherms with the density series equation:

$$\frac{pV}{nRT} = 1 + (\frac{n}{V})B + (\frac{n}{V})^2 C \qquad (3.13)$$

Usually second virial coefficients are calculated from the constant volume apparatus results by assuming that the third virial coefficient is negligible.

3.1.3.4 Differential Pressure Method

Low-pressure experiments of a relative nature are one of four types. In each case the sample gas behaviour is compared with that of a reference gas whose equation of state is well known in the pressure and temperature range of the experiment. The four types of experiment are: (1) at constant volume the difference in pressure is measured after the same change in temperature for each gas; (2) at constant temperature the pressure difference is measured after the two gases are expanded to equal volumes; (3) after expanding the two gases, initially at the same pressure and volume, at constant temperature to equal pressures the difference in volume is measured, and (4) at constant temperature the pressure of each gas is measured at the point where they have equal densities.

Most of the relative p-V-T work is at least as accurate as the absolute p-V-T work because: (1) a great number of the low-pressure experiments are carried out on gases that show large departures from ideality, and (2) the reference gas is usually much more like an ideal gas than is the sample gas. Hence relative results can be readily converted to absolute values with only a small loss in accuracy.

The constant volume gas thermometer has been adapted for relative measurements for second virial coefficients. An apparatus that is essentially two constant volume gas thermometers with independent manometers was developed by Long and Guilbransen (1936) from the single gas thermometer of Giauque, Buttington and Schulze (1927) and Johnston and Weimar (1934). This in turn was developed further by Varehamp and Beenakker (1959), figure 3.11, into a comparative apparatus using an oil-filled manometer. Gases were admitted to each of the constant volume bulbs at the same pressure. The apparatus was then heated by 1 K and the resulting pressure difference read from the differential manometer. They treated their data by using the following equation of state:

$$p = Ad(1 + Bd) \qquad (3.14)$$

where p was the pressure in normal atmospheres,

A was the ratio of the absolute temperature and 273.15,

B was the second virial coefficient,

and d the density expressed in Amagat units.

After denoting the reservoirs 1 and 2 with the initial and final states i and f respectively, an expression of $p_1^i p_2^f / p_2^i p_1^f$ provides the result that

$$\frac{\Delta p}{p_1^f} = (B_2^f - B_2^i)d_2 - (B_1^f - B_1^i)\, d_1 \qquad (3.15)$$

where the gas 1 is the reference gas.

This apparatus was used at low temperatures by Beenakker et al. for studies of H_2, HD and D_2 and their mixtures with He as well as the difference between the second virial coefficients of the ortho and para forms of H_2 and D_2.

Another method starts with two gases in equal volumes at equal pressures, then changes the temperature. The pressure is then equalised by adjusting the amount of mercury confining one of the gases. As with the previous method, this gives a value of $\Delta B/\Delta T$ which requires an absolute value of the second virial coefficient of the sample gas to convert the results into a B versus T plot. Bottomley and Spurling (1964) used an apparatus which Bottomley (1960) first proposed to determine the second virial coefficient of n-butane with this type of method.

3.1.3.5 Differential Compression

In the methods described in the previous section, the temperature was changed at constant volume. In the methods described in this section, the temperature is maintained constant while the gases are compressed to equal volumes. Hamann and Pearse (1952) and Hamann and McManamey (1953) used an apparatus which consists of two similar burettes connected to the opposite sides of a differential manometer. A reference gas is confined in one burette while the sample gas is confined in the other. By changing the mercury levels in each burette the two gases can be compressed to equal

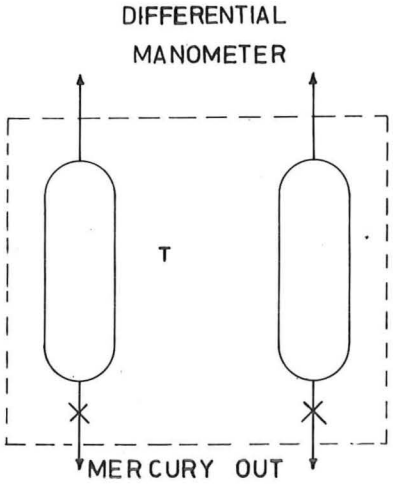


FIGURE 3.13 - DIFFERENTIAL EXPANSION APPARATUS

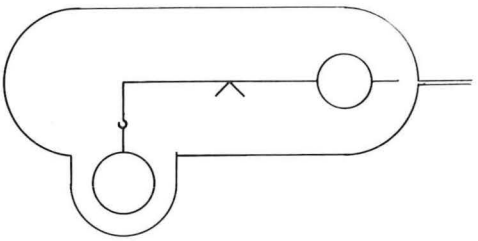


FIGURE 3.14 - GAS DENSITY BALANCE

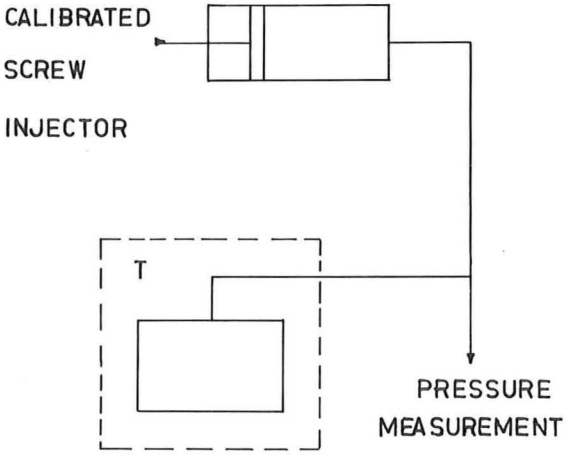


FIGURE 3.15- HIGH PRESSURE p-V-T-n APPARATUS

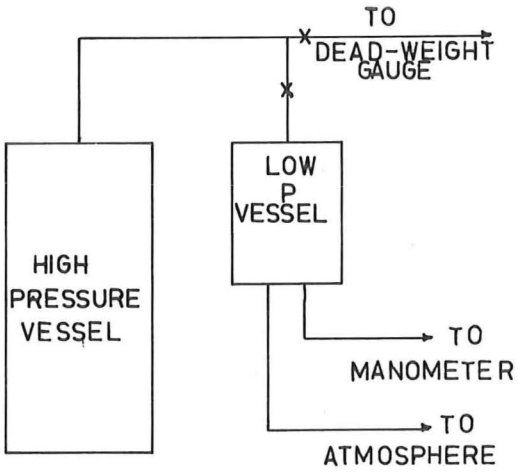


FIGURE 3.16 - BEAN APPARATUS

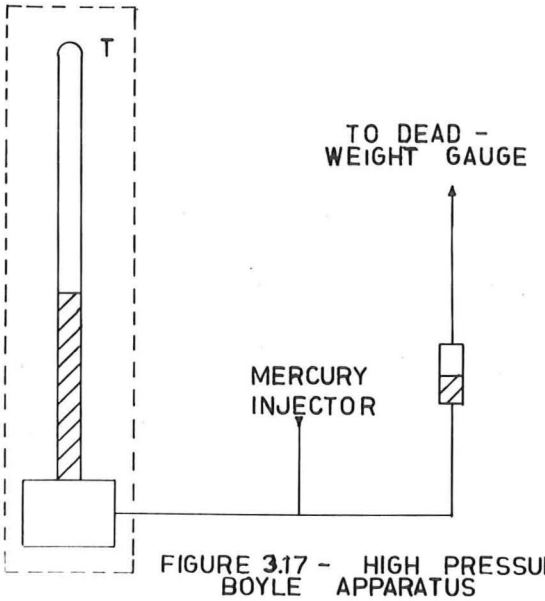


FIGURE 3.17 - HIGH PRESSURE BOYLE APPARATUS

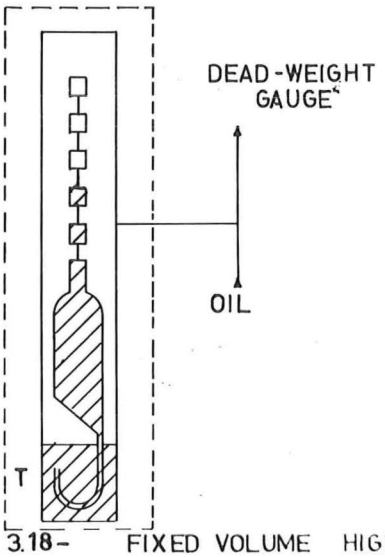


FIGURE 3.18 - FIXED VOLUME HIGH PRESSURE BOYLE APPARATUS

volumes. The differential manometer is used to measure the pressure difference between the two gases.

This type of apparatus, which has also been used by McGlashan and Potter (1962), usually has three bulbs whose volumes do not need to be known. Only ratios of the volumes need be known. This apparatus also suffers from the limits of the temperature range placed on it by the use of mercury for the compressions. From the two compressions using this apparatus, shown in figure 3.12; from where the gases are occupying all three bulbs to where they occupy only one bulb after successive compressions, two second virial coefficients may be calculated. McGlashan and Potter (1962) have determined a final value of the second virial coefficient, B, by using the weighting

$$B = \frac{1}{3}(B_{12} + 2B_{13}) \qquad (3.16)$$

where B_{12} is the virial coefficient obtained from equations 1 and 2 of the three equations describing the compressions and similarly for B_{13}. This equation provided a weighted average since the random error in B_{12} is about twice that in the corresponding value of B_{13}.

Hamann and Pearse (1952) found that depending on what gas was used for the test gas there was sometimes a marked difference in the two values of the second virial coefficient. They attributed this difference to adsorption effects, section 3.1.2.1, or a contribution from higher virial terms.

3.1.3.6 Differential Expansion

A further variation of differential compressibility techniques is to expand the two gases, initially at the same pressure and volume, to constant pressure by the removal of weighed amounts of mercury. The volume changes which can be calculated from these mercury weights are used to calculate the second virial coefficient. This apparatus is illustrated in figure 3.13.

Thomaes and van Steenwinkel (1960) used this technique at low

temperatures. However, since the mercury volume adjusters were not at these low temperatures for practical reasons some of each of the reference and sample gases were also at the volume adjuster temperature. Another version of this type of apparatus which avoids having some of the gases at a temperature different from that of the main volumes has been used by Bottomley, Reeves and Whytlaw-Gray (1958). The major drawback of this method is that the temperature range is limited by the mercury. A further refinement is that proposed by Kappallo, Lund and Schäfer (1963) which avoids the weighing of large amounts of mercury by expanding the two gases by approximately equal and predetermined amounts and attaining pressure equality by a small volume adjustment.

3.1.3.7 Comparative Gas Density Balance

The gas density buoyancy balance, as illustrated in figure 3.14, can also be used in a comparative way to determine the second virial coefficient of a sample by comparing it with another gas whose equation of state is well known.

The chamber surrounding the buoyancy bulb is filled to a known pressure with the reference gas and the balance brought to a null position. The chamber is then evacuated and refilled with the sample gas to a measured pressure such that the buoyancy bulb is again balanced. Thus both gases have the same densities and temperatures at the measured pressures. This microbalance technique was originally used for the determination of molecular weights, but has now been superseded by other methods. Casado, Massie and Whytlaw-Gray (1951), Hajjar and MacWood (1968) and Wallace, Silberberg and McKetta (1964) have all used the gas density balance developed by Edwards (1917) or modifications of it to determine second virial coefficients. Wallace, Silberberg and McKetta (1964) have used both air and neon as the reference gas for their experiments. The truncated pressure series virial equation, written in terms of the molecular weight of the gas, M, and the density, ρ, is

$$\frac{Mp}{\rho} = RT + B'p \qquad (3.17)$$

Explicit equations in the densities of each of the gases may be equated which gives a value of the unknown virial coefficient as:

$$B_2 = \frac{RT}{p_2}\left[\frac{M_2 p_2}{M_1 p_1}\left(1 + \frac{B_1 p_1}{RT}\right) - 1\right] \qquad (3.18)$$

where the subscripts 1 and 2 refer to the reference and sample gases respectively.

3.1.4 High Pressure p-V-T Experimental Methods

Because of the increased difficulty in working at high pressures, p-V-T measurements made to determine second virial coefficients are almost all of the direct nature rather than of the relative type.

3.1.4.1 p-V-T-n Methods

One of the simplest methods of obtaining p-V-T-n data is to fill a container of known volume with a weighed amount of sample and measure the pressure and temperature. Although this particular method has been used at low pressures it is not used very frequently at high pressures. However, Benedict (1937) used this type of method for his temperature-density measurements with nitrogen.

An apparatus in which the volume and temperature are held constant while additional sample is injected into the pressure vessel and the pressure measured has been used by Kell and Whalley (1965) and Kell and McLaurin (1969) to determine the compressibilities of steam and methyl alcohol at high temperatures and pressures, figure 3.15.

A more common method of determining second virial coefficients at high pressures is to load a constant volume vessel with a known amount of sample and to measure the pressure at various temperatures. Hou and Martin (1959) have used this type of experimental technique to determine p-V-T data for trifluoromethane. With this apparatus the amount of sample contained in the loading device is known before loading the vessel. After loading the pressure vessel the amount left in the sample container

and in the loading lines is determined in order to ascertain the amount in the pressure vessel. After the pressure-temperature runs the sample is recovered and weighed as a check on the initial determination.

An alternative procedure for determining the amount of sample in the fixed volume is to expand it to about one bar and measure the pressure. This procedure determines the normal volume - that is, the volume occupied by the mass of gas at a standard temperature and pressure where the equation of state is well known, which is usually $0^{\circ}C$ and about one bar. Corrections need to be made for sample gas contained in the dead spaces of both the high-pressure vessel and the normal volume apparatus. Experiments have been performed using this constant-volume, normal-volume technique by many groups including: David and Hamann (1953), Abraham and Bennett (1960) and Straty and Prydz (1970).

A variation on the previous method has been used by White, Rubin, Camky and Johnston (1960) in the low temperature region to measure the second virial coefficient of helium. At the completion of the pressure-temperature measurements a valve was closed isolating the test vessel after which the gas in the dead spaces was pumped away. The sample still remaining in the pressure vessel was then expanded to low pressure to determine the amount of gas.

A further variation on the constant-volume, normal-volume technique is that used by Nichels, Wassenaar and Zwietering (1952). Other groups have generally used mercury-filled devices to ensure that the constant volume remains constant and to separate the sample gas from the oil of a free-piston gauge but Michels et al. have used a null pressure-indicating diaphragm.

A method developed by Bean, and bearing his name, expands a gas from a high-pressure bomb of known volume into a calibrated burette at about atmospheric pressure. The apparatus is shown in figure 3.16. This method is described by Bloomer (1952) and Solbrig and Ellington (1963). The quantity of gas can be determined from a summation of the increments

measured at low pressure. This procedure differs from the Burnett method (section 3.1.4.4) in that for each expansion the pressure is decreased by about equal increments while in the Burnett method the pressure is halved on each expansion. A plot of pv versus p will yield a value of the second virial coefficient as given in the truncated pressure series:

$$pv = RT + B'p \qquad (3.19)$$

3.1.4.2 Boyle Type Compressions

The variation in compression methods used at high pressures for determining second virial coefficients is not very great. The simplest free compression type of apparatus in which a sample is compressed by mercury inside a capillary tube was used by Connolly and Kandalic (1960), figure 3.17. The volume of the sample gas was determined by sighting on the mercury interface in a calibrated capillary with a cathetometer allowing for meniscus effects and the expansion of the glass. Walters and Smith (1952) determined the position of the mercury/sample gas interface by using a resistance wire placed along the length of the capillary with a small float to sit on the mercury surface. The technique used by a number of research groups including Day and Felsing (1952) and Cherney, Marchman and York (1949) determines the volume of the gas by measuring the amount of mercury that is used to compress the gas. This method has been used at up to 1500 bars.

Similar to the free volume type of compression apparatus is the fixed volume compression apparatus used by Schamp, Mason, Richardson and Altman (1958) and Michels, Michels and Wouters (1935), figure 3.18. The gas burette consists of a number of calibrated bulbs connected by capillary tubes into which the sample gas is compressed. The mercury or oil compressing fluid also surrounds the burette so that there is no pressure difference across it.

Data from these types of experiments are usually fitted to an equation of the form:

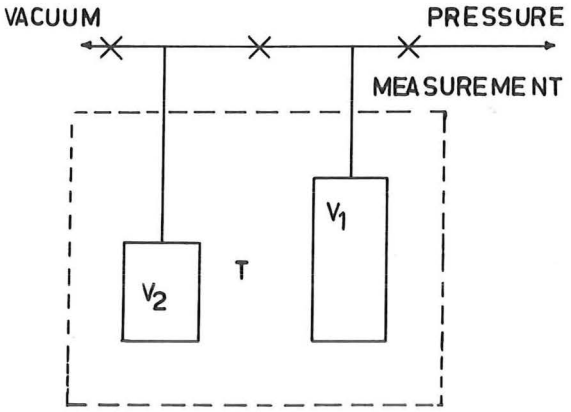


FIGURE 3.19- BURNETT APPARATUS

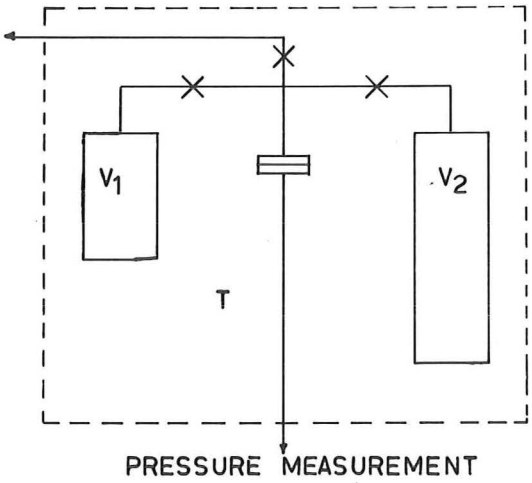


FIGURE 3.20- MODIFIED BURNETT APPARATUS

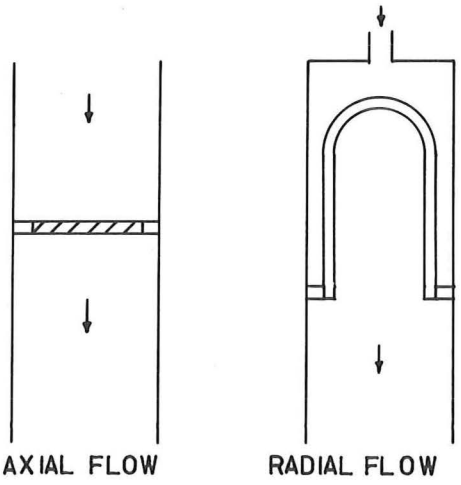


FIGURE 3.21- POROUS PLUGS

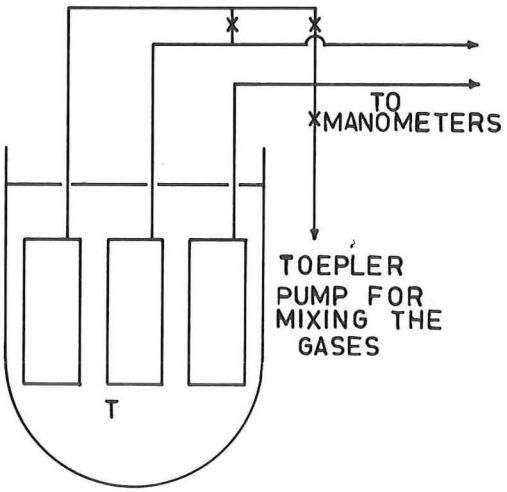


FIGURE 3.22 - A GAS MIXTURE APPARATUS

$$pv = RT(1 + B\rho + C\rho^2) \qquad (3.20)$$

3.1.4.3 Constant Volume Gas Thermometer

Constant volume gas thermometers have been used very infrequently at high pressures for the determination of second virial coefficients (Cox and Lawrenson (1973)).

3.1.4.4 Burnett Method

A method that has found use, mainly in North America, for the determination of second virial coefficients is that developed by Burnett (1936) in 1936. In this type of apparatus, shown in figure 3.19, the sample is put into the first of two fixed but different volumes. The pressure is measured. The valve connecting the two volumes is opened and the sample is allowed to attain equilibrium within the now increased volume. Once the pressure reading is taken the valve is closed and the gas in the second volume is pumped away leaving the volume evacuated. The remaining sample gas which is now contained wholly in the first volume is once again allowed to expand to occupy the two volumes when the pressure is measured a further time. This operation is repeated until the pressure becomes too low for accurate measurements to be taken. The advantages of this method are: (1) that accurate volume determinations are not necessary, (2) there is no need to measure the amount of gaseous sample in the apparatus, (3) the apparatus is mercury free and can therefore be used to relatively high temperatures. However, this method cannot be used in the regions where pV is changing rapidly with p, in the liquid or two-phase region or near the saturated vapour pressure. Although this method has not found widespread use, there are available Burnett apparatus' from a few commercial manufacturers of instruments.*

*Chandler Engineering Company, Oklahoma, U.S.A.
Ruska Instrument Corporation, Texas, U.S.A.

The virial equation can be written in terms of compressibilities:

$$z = \frac{pV}{nRT} = 1 + B'p + C'p^2 + \ldots \tag{3.21}$$

and if we define the Burnett apparatus constant, N, as

$$N = \frac{V_1 + V_2}{V_1} \tag{3.22}$$

then after the xth expansion the pressure in the combined volume is p_x and

$$p_x(V_1 + V_2) = z_x n_x RT \tag{3.23}$$

But before the xth expansion when the sample is confined to volume V_1:

$$p_{x-1}V_1 = z_{x-1}n_{x-1}RT \tag{3.24}$$

and since $n_{x-1} = n_x$, then

$$\frac{p_{x-1}V_1}{p_x(V_1+V_2)} = \frac{z_{x-1}}{z_x} \tag{3.25}$$

hence

$$\frac{p_{x-1}}{p_x} = N\frac{z_{x-1}}{z_x} \tag{3.26}$$

For the first x expansions there are similar expressions for each and combined they yield:

$$\frac{p_o}{p_x} = N^x\frac{z_o}{z_x} \tag{3.27}$$

where the subscript, o, indicates the initial condition. A plot of $\frac{p_x}{p_{x-1}}$ versus p_x provides a value of the apparatus constant. However, extrapolation over wide pressure ranges could give rise to an inaccurate value of N since errors in z_{k-1} are introduced into z_k and so on. In order to avoid this problem it has been suggested that the apparatus constant be obtained from an experiment done with a perfect gas, such as helium, where a plot of p_x/p_{x-1} versus p_x will be very nearly linear. The only disadvantage with this procedure is that it assumes that the apparatus constant will not change with time.

The basic Burnett equations, which are usually written in terms of

compressibilities, can also be written in terms of the symbols of the virial equation truncated to the second term.

$$pV = n(RT + B'p) \tag{3.28}$$

Before the first expansion from the first vessel we have:

$$\frac{p_o V_1}{n_o} = RT + B'p_o \tag{3.29}$$

After the first expansion when both vessels are at the same pressure, p_1:

$$\frac{p_1(V_1 + V_2)}{n_o} = RT + B'p_1 \tag{3.30}$$

From the latter two equations we have:

$$\frac{p_o}{p_1} = N + (N - 1)\frac{B'}{RT}p_o \tag{3.31}$$

For each expansion an equation of this form may be written such that a plot of p_j/p_{j+1} versus p_j will have a slope of $\frac{B'}{RT}(N-1)$ and an intercept at $p_j = 0$ of N. Having determined a value of N the second virial coefficient, B', may then be calculated from the slope.

The Burnett method in its basic form has been used by a number of workers, among them being: Anderson, Kudchadker and Eubank (1968), Hirth and Kobe (1961) and Moreland, McKetta and Silberberg (1967). Hall and Eubank (1974) have suggested a variation, figure 3.20, which they claim offers a number of advantages over the conventional Burnett apparatus, the main one being that of simplicity.

3.1.5 Other Experimental Methods

All of the experimental methods mentioned previously determine second virial coefficients by measuring p-V-T properties. One of the major difficulties in direct p-V-T measurements is that of calibrating and measuring volumes. This can be surmounted by the measurement of some other intrinsic property which depends on gas non-ideality.

3.1.5.1 Sound Velocity

The velocity of sound is a property that depends on real gas behaviour. Measuring the velocity of sound at constant temperature and at a series of pressures from which second virial coefficients may be calculated avoids the measurement of volume.

A low amplitude, variable frequency signal, emitted at one end of a closed resonance tube with fixed ends and reflected at the other, defines a sequence of standing waves which permits calculation of the sonic velocity in the confined gas at a given temperature and pressure.

The velocity of sound in a real gas may be described by the equation:

$$c^2 = A_o + A_1 p + A_2 p^2 \qquad (3.32)$$

where A_o is the velocity of sound in a perfect gas, squared, and A_1 is giben by

$$A_1(T) = \frac{\gamma_o}{M}\left[2B(T) + \frac{4}{3}T \frac{dB}{dT} + \frac{4}{15} T^2 \frac{d^2B}{dT^2} \right] \qquad (3.33)$$

where γ_o is the ratio of the heat capacity at constant pressure to that at constant volume, and M is the molar mass.

At low temperatures, where these sound velocity measurements are usually carried out, the temperature dependence of the second virial coefficient can be represented, Williamson (1964) by the relation:

$$B(T) = \alpha + \beta/T \qquad (3.34)$$

where α and β are constants. Hence: $A_1(T) = \frac{\gamma_o}{M}(2\alpha + \frac{6B}{5T})$. (3.35)

A plot of A_1 from the sound velocity measurements versus T^{-1} will yield values of α and β from which second virial coefficients may be found.

This method has been used by Grimsrud and Werntz (1967) for the determination of second virial coefficients of helium.

3.1.5.2 Refractive Index

Measurements of refractive index at constant temperature can be used to determine second virial coefficients as shown by Ashton and Guggenheim (1956). One cell of a Rayleigh interference refractometer is kept

evacuated while the other is filled with the sample gas at a measured pressure. A small amount of the sample gas is bled out of the cell and the pressure measured while the number of rings displaced is counted. This procedure is followed until the sample gas is all removed from the cell in which it was kept. The rrefractive index, n, is given by:

$$(n-1) = \frac{x\lambda}{L} \tag{3.36}$$

where x is the number of fringes displaces,

λ is the wavelength of the light source used, in a vacuum,

L is the length of the refractometer tube.

Using the relation for the molar polarisation, P,

$$P = \left[\frac{n^2 - 1}{n^2 + 2}\right] v \tag{3.37}$$

where v is the molar volume, and P may be expressed as a function of density by the relation

$$P = P^o \left(1 + \frac{\beta}{v} + \ldots\right) \tag{3.38}$$

where P^o is the limiting value of P at zero density and β is the refractivity second virial coefficient which is a function of temperature. Substitution of this into the virial equation

$$pv = RT\left(1 + \frac{B}{v}\right) \tag{3.39}$$

gives

$$\left[\frac{n^2-1}{n^2+2}\right] \frac{RT}{p} = P^o \left(1 + \frac{\beta-B}{v}\right) \tag{3.40}$$

Since β is less than the experimental error of B, the equation may be written as:

$$\left[\frac{n^2-1}{n^2+2}\right] \frac{RT}{p} = P^o\left(1 - \frac{Bp}{RT}\right) \tag{3.41}$$

and hence B may be calculated from measurements of refractive index and pressure.

3.1.5.3 Joule-Thomson Coefficients

The Joule-Thomson coefficients, both isothermal and isenthalpic, have been used to determine second virial coefficients. These methods have the advantage that unlike the direct methods they do not measure differences between two large numbers. Also there is no adsorption problem associated with this type of method. The isenthalpic coefficient $(\frac{\partial T}{\partial p})_H = \mu$, is related to the isothermal coefficient, $(\frac{\partial H}{\partial p})_T = \phi$, by the relationship

$$\phi = - \mu C_p \qquad (3.42)$$

Francis, McGlashan and Wormald (1969) and Charnley, Isles and Townley (1953) have measured isothermal Joule-Thomson coefficients by passing the test gas through a valve or porous plug. The gas flows through the throttle at a known flow rate with the initial temperature being measured. The gas temperature changes as it flows through the throttle but on the downstream side it is heated or cooled to attain its original temperature, with the amount of energy required to do this being measured. The pressure drop across the throttle is also measured. The isothermal Joule-Thomson coefficient, ϕ, is given by:

$$\phi = \frac{H(p_2) - H(p_1)}{p_2 - p_1} = \frac{1}{p_2 - p_1} \int_{p_1}^{p_2} \left[v - T(\frac{\partial v}{\partial T})_p \right] dp \qquad (3.43)$$

where the subscripts 1 and 2 refer to the upstream and downstream sides of the throttle.

If the equation of state is written as:

$$pv = RT + B'p + (C - B'^2)p^2/RT \qquad (3.44)$$

then from the two latter equations and the integration

$$\phi = (B' - T\frac{dB'}{dT}) + \tfrac{1}{2}(p_1 + p_2)(C' - T\frac{dC'}{dT}) \qquad (3.45)$$

where $C' = (C - B'^2)/RT$.

On a plot of the measured quantity, ϕ, versus $\frac{1}{2}(p_1 + p_2)$, the intercept at $\frac{1}{2}(p_1 + p_2) = 0$ is $B' - T\frac{dB'}{dT}$ and the initial slope is $C' - T\frac{dC'}{dT}$. From the values of the intercepts, a graph of $B' - T\frac{dB'}{dT}$ versus T was plotted to which was fitted a curve of the form

$$B = X + Y e^{z/T} \tag{3.46}$$

where X, Y and z are constants. The values obtained by Francis, McGlashan and Wormald (1969) using this method agreed well with values in the literature obtained by direct p-V-T measurements.

The adiabatic Joule-Thomson coefficient, $(\frac{\partial T}{\partial p})_H$, is determined by measuring the temperature difference across a throttling device at a constant pressure drop. There are three types of throttling devices that have been used for this: valves or orifices, axial-flow porous plugs, and radial-flow porous plugs.

The valve or an orifice, which was initially used for the determination of Joule-Thomson coefficients, has not been used as frequently as either of the porous plugs, both of which are shown in figure 3.21. These devices can be easily constructed but one of their major drawbacks is that of heat leaks. This problem can, to a certain extent, be overcome by constructing the throttle from thermally non-conducting material as did Johnson (1946). Patee and Brown (1934) and Stockett and Wenzel (1964), among others, have used these devices for determining Joule-Thomson coefficients.

The axial-flow porous plug still has a heat leak problem as does the valve but this leakage is not as great as for the valve. The only advantage that an axial-flow porous plug has over the radial-flow porous plug is that of ease of fabrication, as pointed out by King and Potter (1962).

Most of the experimental Joule-Thomson coefficients are measured using a radial-flowporous plug. Burnett (1923) and Sage, Kennedy and Lacey (1936) used this type of device. While the axial-flow porous plug has a reduced heat loss when compared with the valve, the radial-flow

porous plug is better still.

Since $\phi = -\mu Cp$, then

$$\mu = \frac{1}{Cp}\left(B' - T\frac{dB'}{dT}\right) \qquad (3.47)$$

if the third and higher virial coefficients are considered to be negligible.

3.1.5.4 Rapid Compressions/Expansions

Devices developed by Slawsky, Seigel, Ho, Kopp and Van der Slice (1959) have been usedto study gas behaviour. They observed the behaviour of gases undergoing rapid dynamic processes, either compressions or expansions. The data obtained initially from these devices are isentropic pressure-density curves.

3.1.5.5 Nuclear Magnetic Resonance

It has been suggested by Lipsicas, Bloom and Muller (1961) that nuclear magnetic resonance measurements can be used for obtaining the compressibilities of gases whose nuclei have a non-zero spin. This technique uses a reference gas whose compressibility is well known at the conditions of the experiment and in the same apparatus to obtain the apparatus constant. Although not providing extremely accurate compressibility data for the test gas (of the order of a few percent) it could be useful for obtaining p-V-T data where speed rather than accuracy is important.

3.1.5.6 Clapeyron Equation

It is possible to determine second virial coefficients from a combination of vapour pressure measurements and the latent heat of vaporisation using the Clapeyron equation. This method is most useful when the nature of the substance makes it unsuitable to use one of the more usual methods. The Clapeyron equation is:

$$\frac{dp}{T} = \frac{\Delta H}{T\Delta v} \qquad (3.48)$$

where $\Delta v = v_g - v_l$ and is the molar volume change on vaporisation while v_g and v_l are the molar volumes of the gas and liquid phases

respectively. Substituting for v_g from the truncated pressure series virial equation, the Clapeyron equation becomes:

$$B' = \frac{\Delta H}{T}\frac{dT}{dp} + v_l - \frac{RT}{p} \qquad (3.49)$$

Ashton, Finke, Bestul, Pace and Szasc (1946) have used this equation to determine second virial coefficients of but-1-ene. A curve was fitted to the vapour pressure-temperature data after which it was differentiated and the slope evaluated at various temperatures. From data that were available the molar latent heat of vaporisation was known. This information was substituted into the above equation to yield a value of B'.

During experiments to determine the heat of vaporisation, it is not unusual to measure also the vapour heat capacity as a function of temperature. These values can be used as a check on the values of the second virial coefficients through the relation

$$\left(\frac{\partial Cp}{\partial p}\right)_T = -T\left(\frac{d^2B}{dT^2}\right) \qquad (3.50)$$

There have been a large number of publications containing second virial coefficients from the experimental work of McCullough and his co-workers using this technique, for example: McCullouch, Scott, Finke, Gross, Williamson, Pennington, Waddington and Huffman (1952), Waddington, Todd and Huffman (1947), McCullough, Scott, Pennington, Hossenlopp and Waddington (1954) and McCullough, Pennington and Waddington (1952).

3.2 Experimental Methods for the Determination of Virial Coefficients of Gaseous Mixtures

All of the experimental techniques described in the previous sections may be used to determine the second virial coefficient of mixtures. There are, however, a few methods that are applicable only to gas mixtures.

Differential p-V-T methods: One interaction virial coefficient method, used by Knobler, Beenakker and Knaap (1959), is shown in figure 3.22 where two pure gases were initially held at the same pressure in two

of the bulbs of the apparatus. A third reference bulb was also held at this pressure while all three were held at constant temperature. The two bulbs in which the pure gases were held were connected and the contents mixed, after which the resulting pressure was compared with that in the reference bulb. It can be shown that

$$\frac{\Delta p}{p_i} = \frac{\rho_2 E}{2(1 + B_{11}\rho_1)} + \frac{(\rho_2 - \rho_1)^2}{4\rho_1\rho_2} \qquad (3.51)$$

where p_i is the initial pressure,

Δp is the pressure change on mixing,

ρ_1 and ρ_2 are the pure component densities,

B_{11} is the virial coefficient of pure component 1

and E is an excess quantity defined by:

$$E = B_{12} - \frac{1}{2}(B_{11} + B_{22}) \qquad (3.52)$$

in which B_{22} is the virial coefficient of pure component 2 and B_{12} is the interaction virial coefficient.

A similar method, used by Edwards and Roseveare (1942), measures the volume change on mixing. The value of the second virial coefficient is given by:

$$\frac{\Delta V}{n(x_1 x_2)} = 2\left[B_{12} - \frac{1}{2}(B_{11} + B_{22}) \right] \qquad (3.53)$$

where ΔV is the volume change on mixing at constant pressure and n is the total number of moles in the system, x_1 and x_2 are the mole fractions of the two gases, while B_{11} and B_{22} are the pure component virial coefficients, if the virial equation of state is truncated at the second virial coefficient.

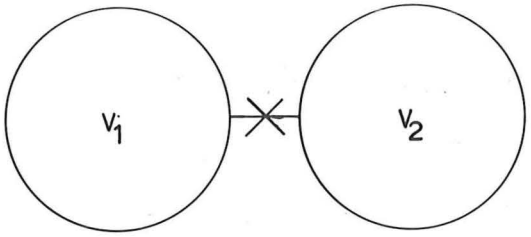
Solubility method: When a solid or liquid is placed in contact with a compressed gas some of the liquid or solid forms a binary mixture with the gas. The deviations from ideal solubility of the solid and the gas are measured and the second virial coefficient calculated after making corrections for the amount of gas that has become dissolved in the solid or liquid. Kretschmer and Wiebe (1951) have used this method for the

solubility of propane and butane in ethanol. The second virial coefficient may be found from the equation:

$$\ln \left(\frac{c_2}{c_2^o}\right) = \frac{v_2 - 2B_{12}}{v} + \ldots \qquad (3.54)$$

where c_2/c_2^o is the ratio of the vapour concentrations in the presence and absence respectively of the compressed gas, v_2 is the molar volume of the condensed phase, and v is the molar volume of the gas mixture. A plot of v versus $\ln(c_2/c_2^o)$ will provide a value of B_{12}. Najour and King (1966) have used this method to find the virial coefficient of mixtures of naphthalene with methane, ethylene and carbon dioxide. The concentration of the naphthalene in the various compressed gases was determined spectrophotometrically.

Chromatography measurements: A relatively new experimental technique for determining mixed second virial coefficients is that suggested by Everett and Stoddart (1961) which has subsequently been used by a number of other workers; for example: Cruickshank and Young (1966) and Vigdergauz and Semkin (1971). This experimental technique uses gas-liquid chromatography to provide the data from which the second virial coefficients are calculated. A logarithmic function of the retention volume is extrapolated to zero pressure. The intercept, the net retention volume at zero pressure, is related to the second virial coefficient of the mixture, B_{12}.



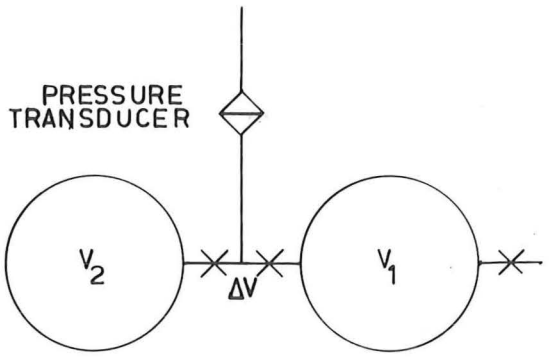
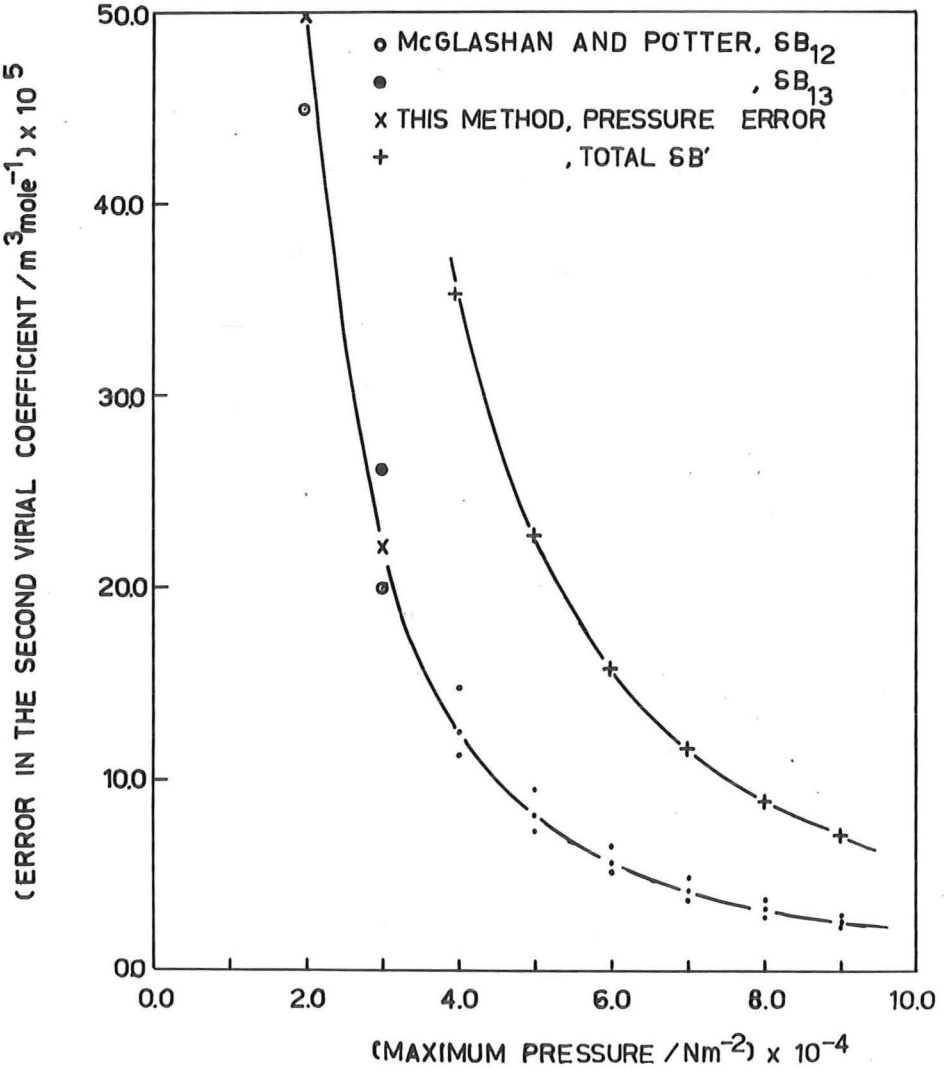


FIGURE 4.1 - SIMPLIFIED APPARATUS FIGURE 4.2 - BASIS OF APPARATUS

FIGURE 4.3

ERROR IN THE SECOND VIRIAL COEFFICIENT VERSUS PRESSURE AT 300K



4. THE PROPOSED METHOD

4.1 Introduction

The experimental virial coefficient work in the Department of Chemical Engineering was commenced by Dr S.P. O'Neil who built a crude version of the apparatus described here from which he obtained some rough results. These were very badly scattered but they provided the impetus to carry on with this work. Dr M.V. Pandya built an improved version of the apparatus and obtained the results which are included with all the other second virial coefficients in figure 6.5. These results looked most promising but varied from the generally accepted values sufficiently to warrant further investigation. The apparatus described here is a redesigned and rebuilt version of that used by Pandya with some improvements such as keeping the central valve arrangement out of contact with the oil bath oil.

4.2 Outline of the Proposed Method

Consider a simple apparatus consisting of two bulbs connected with a valve in between as shown in figure 4.1. A sample is loaded into volume 1 where its pressure is measured. The gas is then expanded to fill both volumes and its pressure is again measured. A third pressure measurement is made with all of the sample contained in volume 2. At each pressure a truncated pressure series virial equation can be written as shown below.

$$p_1V_1 = nRT + nB'p_1 + nC'p_1^2 \qquad (4.1)$$

$$p_2V_2 = nRT + nB'p_2 + nC'p_2^2 \qquad (4.2)$$

$$p_3(V_1+V_2) = nRT + nB'p_3 + nC'p_3^2 \qquad (4.3)$$

By substituting the values of V_1 and V_2 from equations 4.1 and 4.2 respectively into equation 4.3, it becomes:

$$B' + C'(p_1 + p_2 - p_3) = RT\left(\frac{1}{p_3} - \frac{1}{p_1} - \frac{1}{p_2}\right) \qquad (4.4)$$

This can be rewritten as:

$$B'_{apparent} = B' + C'(p_1 + p_2 - p_3) = RT\left(\frac{1}{p_3} - \frac{1}{p_1} - \frac{1}{p_2}\right) \qquad (4.5)$$

It then follows that a plot of $B'_{apparent}$ versus the pressure term $(p_1 + p_2 - p_3)$ will have an intercept at zero pressure of B' and a slope of C'.

4.3 Detailed Development of the Method and the Equations Used

To measure the three pressures necessary for this method, at constant temperature, and use but one manometer, an additional section is necessary. This consists of a small volume, ΔV, to which is attached a differential pressure transducer and one other valve. This extra section is placed between the two bulbs as shown in figure 4.2.

The condensable gas under investigation was introduced into the first volume while the second was kept evacuated and the pressure of the gas occupying $(V_1 + \Delta V)$ measured. The gas was then allowed to expand to occupy both volumes with the pressure being measured again. The gas was then transferred completely into the second volume, after which the pressure of the gas occupying the volume $(V_2 + \Delta V)$ was measured. After these three pressures were measured with the gas of one loading, more gas was added and the procedure repeated. Successive samples were added until the maximum pressure for each loading approached either one bar or the saturation vapour pressure.

Three truncated pressure series virial equations can be written for each loading of n moles at constant temperature corresponding to the three volumes used.

$$p_1(V_1 + \Delta V) = nRT + nB'p_1 + nC'p_1^2 \qquad (4.6)$$

$$p_2(V_2 + \Delta V) = nRT + nB'p_2 + nC'p_2^2 \qquad (4.7)$$

$$p_3(V_1 + V_2 + \Delta V) = nRT + nB'p_3 + nC'p_3^2 \qquad (4.8)$$

By eliminating V_1 and V_2 from equations 4.6, 4.7 and 4.8, an equation similar to the simple expression of equation 4.4 can be obtained as follows:

$$B' + C'(p_1 + p_2 - p_3) = RT\left(\frac{1}{p_3} - \frac{1}{p_1} - \frac{1}{p_2}\right) + \frac{\Delta V}{n} \qquad (4.9)$$

$$\text{If } B'_{apparent} \equiv RT\left(\frac{1}{p_3} - \frac{1}{p_1} - \frac{1}{p_2}\right) + \frac{\Delta V}{n} \qquad (4.10)$$

$$\text{then } B'_{apparent} = B' + C'(p_1 + p_2 - p_3) \qquad (4.11)$$

$$\text{and } B' = \underset{(p_1+p_2-p_3)\to 0}{Lt} B'_{apparent} \qquad (4.12)$$

Consequently a plot of $\left(RT\left(\frac{1}{p_3} - \frac{1}{p_1} - \frac{1}{p_2}\right) + \frac{\Delta V}{n}\right)$ versus $p_1 + p_2 - p_3$ yields B' as the intercept and C' as the limiting slope of the plot.

If the term in C and all higher terms of the density series virial equation are zero, then the three equations applicable to each loading of the apparatus are as follows:

$$p_1 = \left(\frac{n}{V_1 + \Delta V}\right)RT + \left(\frac{n}{V_1 + \Delta V}\right)^2 BRT \qquad (4.13)$$

$$p_2 = \left(\frac{n}{V_2 + \Delta V}\right)RT + \left(\frac{n}{V_2 + \Delta V}\right)^2 BRT \qquad (4.14)$$

$$p_3 = \left(\frac{n}{V_1 + V_2 + \Delta V}\right)RT + \left(\frac{n}{V_1 + V_2 + \Delta V}\right)^2 BRT \qquad (4.15)$$

After eliminating V_1 and V_2 from these equations, an iterative process was used that chose an initial value of B, decided if this value satisfied the resulting equation and then chose a better value of B. The procedure was then repeated until the chosen value of B satisfied the equation. Similarly to the pressure series case a value of the "true" second virial coefficient can be found by plotting these density series virial coefficients against $(p_1 + p_2 - p_3)$ and extrapolating to zero pressure.

If either of the pressure or density series virial equations is inverted into the other and coefficients equated, then the following results are obtained:

$$B = B' \qquad (4.16)$$

$$\text{and } C = B'B + C'RT = B^2 + C'RT \qquad (4.17)$$

Hence, in both of the analyses described a value of the second virial coefficient is obtained by extrapolating to zero pressure. Therefore a test of the accuracy of this method would be coincident intercepts.

4.4 Error Analysis

The three truncated pressure series equations relevant to this method are of the type

$$p_i V_i = nRT + nB'p_i \tag{4.18}$$

where i = 1, 3 corresponding to the sample gas confined in volume 1, volume 2 and spread between both volumes respectively. An equation incorporating the errors can also be written in the form:

$$(p_i + \delta p_i)(V_i + \Delta V + \delta V_i) = (n + \delta n_i)R(T + \delta T_i) + (n + \delta n_i)B'(p_i + \delta p_i) \tag{4.19}$$

where δp_i is the observation error in the pressure measurement

δV_i is allowing for any change in volume such that the sum of V_1 and V_2 does not equal V_3

δn_i is a change in the amount of gas present because of adsorption effects or incomplete distillations.

To a first approximation this becomes

$$p_i V_i + p_i \Delta V + p_i \delta V_i + V_i \delta p_i + \Delta V \delta p_i = nRT + nR\delta T_i + \delta n_i RT + nB'p_i + nB'\delta p_i + \delta n_i B p_i \tag{4.20}$$

By adding to the equation in which i = 1, the equation where i = 2 and subtracting from the sum the equation in which i = 3, the following result is obtained:

$$\begin{aligned} B' = \{ & RT\left(\frac{1}{p_3} - \frac{1}{p_2} - \frac{1}{p_1}\right) + \frac{\Delta V}{n} - \frac{1}{n}(\delta V_3 - \delta V_2 - \delta V_1) - \frac{1}{n}\left(\frac{V_3 \delta p_3}{p_3} - \frac{V_2 \delta p_2}{p_2} - \frac{V_1 \delta p_1}{p_1}\right) \\ & - \frac{\Delta V}{n}\left(\frac{\delta p_3}{p_3} - \frac{\delta p_2}{p_2} - \frac{\delta p_1}{p_1}\right) + R\left(\frac{\delta T_3}{p_3} - \frac{\delta T_2}{p_2} - \frac{\delta T_1}{p_1}\right) + \frac{RT}{n}\left(\frac{\delta n_3}{p_3} - \frac{\delta n_2}{p_2} - \frac{\delta n_1}{p_1}\right) \\ & + B'\left(\frac{\delta p_3}{p_3} - \frac{\delta p_2}{p_2} - \frac{\delta p_1}{p_1}\right) + \frac{B'}{n}(\delta n_3 - \delta n_2 - \delta n_1) \end{aligned} \tag{4.21}$$

If it is assumed that $|\delta V_3| = |\delta V_2| = |\delta V_1|$

$$|\delta p_3| = |\delta p_2| = |\delta p_1|$$

$$|\delta T_3| = |\delta T_2| = |\delta T_1|$$

$$|\delta n_3| = |\delta n_2| = |\delta n_1|$$

and expressing the error equation in terms of the highest pressure, p_1, and the corresponding volume, V_1, we obtain

$$B'_{obs} = B'_{real} \pm \frac{3\Delta V}{n} \pm \frac{\delta p}{np}(6V + 4\Delta V) \pm \frac{4\delta TR}{p} \pm \frac{RT}{pn}(2\delta n_3 - 2\delta n_1) \pm \frac{4B'\delta p}{p} \pm \frac{B}{n}(2\delta n_3 - 2\delta n_1) \quad (4.22)$$

where B'_{obs} is the value of B' calculated from the experimentally measured quantities, and B'_{real} is the error-free second virial coefficient.

Hence

$$\delta B'_{max} \approx \frac{6\delta pV}{np} + \frac{4\delta TR}{p} + \frac{RT}{pn}(2\delta n_1 - 2\delta n_3) + \frac{4B'\delta p}{p} + \frac{B'}{n}(2\delta n_1 - 2\delta n_3) \quad (4.23)$$

since $\frac{3\delta V}{n}$ and $\frac{4\delta p\Delta V}{np}$ are negligible.

To the extent that the approximation $pV \approx nRT$ is valid, then this maximum error becomes:

$$\delta B'_{max} \approx \frac{6RT\delta p}{p^2} + \frac{4\delta TR}{p} + \left(\frac{RT}{p}\right)^2 \frac{2}{V}(\delta n_1 - \delta n_3) + \frac{4B'\delta p}{p} + \frac{2B'RT}{pV}(\delta n_1 - \delta n_3) \quad (4.24)$$

Distillation error: When adding a sample to the apparatus during an experimental run, the degree of completion of any distillation could be observed on the Pirani gauge. For any addition, the maximum increase in pressure at the end of the distillation was 0.4 N m^{-2}. This corresponds to a δn of about 3×10^{-7} moles.

Pressure reading error: For any one reading, the cathetometer could be read to within ±2.65 N m^{-2} which then contributes an error of ±5.3 N m^{-2}. The coefficient of linear expansion of silica glass as given by Perry (4th edition) is of the order of 4×10^{-7} K^{-1}. The silica glass scale was calibrated at 20°C and for a very extreme case of a reading being taken at 30°C an error of 0.4 N m^{-2} on a pressure of 0.8×10^5 N m^{-2} is introduced. This is negligible in relation to this experiment considering the extremeness of this case. Zero variations of the pressure transducer, which were checked at the completion of each experimental run, were of the order of 4.0 N m^{-2}. Hence the total maximum pressure reading error was 9.3 N m^{-2}.

Temperature error: Over a period of several days the maximum change in temperature of the oil bath, as shown by a Beckmann thermometer, was 0.04 K.

The figures in table 4.1 were calculated assuming that: $R = 8.314$ N m mol^{-1} K^{-1}, $T = 300$ K, $B' = -1.5 \times 10^{-3}$ m^3 mol^{-1}, $V = 1.5 \times 10^{-3}$ m^3, $\delta n = 10^{-6}$ mole, $\delta p = 9.3$ N m^{-2}, and $\delta T = 0.02$ K, since over the period of time for the three pressure measurements necessary the temperature did not change by more than this.

These figures in table 4.1 are the maximum possible errors. The probable errors are much less than this. The pressure transducer zero shift has been put at 4.0 N m^{-2} in the analysis but this occurred over a complete run. A probable zero shift over the time necessary for the pressure readings for one value of $B'_{apparent}$ would be 0.65 N m^{-2}. In the measuring of one pressure difference, three readings were taken for each mercury height so that the error in the pressures from which the second virial coefficient was calculated could be divided by $\sqrt{3}$ (Topping (1955)). Since it is most unlikely that each probable error is a maximum all the time, the probable error in B' will be assigned by taking the square root of the sum of the squares of the first two error sources in table 4.1 and adding the remaining contributions. The results are shown in table 4.2.

In their paper, McGlashan and Potter (1962) have plotted expected magnitudes of $|\delta B'|$ versus the starting pressure for each compression. It is of interest to plot the expected values of $\delta B'$ from their work and those for this work. McGlashan and Potter obtained two curves, one for each virial coefficient, based on the starting pressure for each compression. If, however, instead of the starting pressure for each compression, the maximum pressure is used, these two lines become almost coincident. If a smooth line is placed through these two sets of points, the error contribution from the pressure measurement of this work, assuming the same pressure measurement accuracy as McGlashan and Potter, falls exactly on that line as shown in figure 4.3. Although the pressure

measurement error is the major component in the total probable error, there are other uncertainties, as shown in table 4.2, which add to it to make the total probable error. This total probable error is also plotted in figure 4.3.

Table 4.1 Maximum Errors

$p/N\ m^{-2}$	$\frac{6RT\delta p}{p^2}/m^3\ mole^{-1}$	$\frac{4\delta TR}{p}/m^3\ mole^{-1}$	$(\frac{RT}{p})^2\frac{2\delta n}{V}/m^3\ mole^{-1}$	$\frac{4B'\delta p}{p}/m^3\ mole^{-1}$	$\frac{2B'RT\delta n}{pV}/m^3\ mole^{-1}$	$\delta B'_{max}/m^3\ mole^{-1}$
1.0×10^4	139×10^{-5}	6.6×10^{-5}	8.3×10^{-5}	0.56×10^{-5}	0.05×10^{-5}	155×10^{-5}
2.0×10^4	35×10^{-5}	3.3×10^{-5}	2.1×10^{-5}	0.28×10^{-5}	0.03×10^{-5}	41×10^{-5}
3.0×10^4	15×10^{-5}	2.2×10^{-5}	1.1×10^{-5}	0.19×10^{-5}	0.02×10^{-5}	19×10^{-5}
4.0×10^4	8.7×10^{-5}	1.6×10^{-5}	0.5×10^{-5}	0.14×10^{-5}	0.02×10^{-5}	11×10^{-5}
5.0×10^4	5.6×10^{-5}	1.3×10^{-5}	0.3×10^{-5}	0.11×10^{-5}	0.01×10^{-5}	7.3×10^{-5}
6.0×10^4	3.9×10^{-5}	1.1×10^{-5}	0.2×10^{-5}	0.09×10^{-5}	0.01×10^{-5}	5.3×10^{-5}
7.0×10^4	2.8×10^{-5}	0.94×10^{-5}	0.20×10^{-5}	0.08×10^{-5}	0.01×10^{-5}	4.0×10^{-5}
8.0×10^4	2.2×10^{-5}	0.82×10^{-5}	0.10×10^{-5}	0.07×10^{-5}	negligible	3.2×10^{-5}
9.0×10^4	1.7×10^{-5}	0.73×10^{-5}	0.10×10^{-5}	0.06×10^{-5}		2.6×10^{-5}
10.0×10^4	1.4×10^{-5}	0.66×10^{-5}	0.08×10^{-5}	0.06×10^{-5}		2.2×10^{-5}

Table 4.2 Probable Errors

$p/N\ m^{-2}$	$\frac{6RT\delta p}{p^2}/m^3\ mole^{-1}$ (A)	$\frac{4\delta TR}{p}/m^3\ mole^{-1}$ (B)	$\sqrt{A^2+B^2}\ /\ m^3\ mole^{-1}$	$(\frac{RT}{p})^2\ \frac{2\delta n}{V}\ /\ m^3\ mole^{-1}$	$\frac{4B'\delta p}{p}\ /m^3\ mole^{-1}$	$\frac{2B'RT\delta n}{pV}/m^3\ mole^{-1}$	$\delta B'/m^3\ mole^{-1}$
$1.0x10^4$	$55x10^{-5}$	$6.6x10^{-5}$	$56x10^{-5}$	$8.3x10^{-5}$	$0.22x10^{-5}$	$0.05x10^{-5}$	$64x10^{-5}$
$2.0x10^4$	$14x10^{-5}$	$3.3x10^{-5}$	$14x10^{-5}$	$2.1x10^{-5}$	$0.11x10^{-5}$	$0.03x10^{-5}$	$16x10^{-5}$
$3.0x10^4$	$6.0x10^{-5}$	$2.2x10^{-5}$	$6.4x10^{-5}$	$1.1x10^{-5}$	$0.08x10^{-5}$	$0.02x10^{-5}$	$7.6x10^{-5}$
$4.0x10^4$	$3.5x10^{-5}$	$1.6x10^{-5}$	$3.9x10^{-5}$	$0.5x10^{-5}$	$0.06x10^{-5}$	$0.02x10^{-5}$	$4.5x10^{-5}$
$5.0x10^4$	$2.2x10^{-5}$	$1.3x10^{-5}$	$2.6x10^{-5}$	$0.3x10^{-5}$	$0.04x10^{-5}$	$0.01x10^{-5}$	$3.0x10^{-5}$
$6.0x10^4$	$1.6x10^{-5}$	$1.1x10^{-5}$	$1.9x10^{-5}$	$0.2x10^{-5}$	$0.04x10^{-5}$	$0.01x10^{-5}$	$2.2x10^{-5}$
$7.0x10^4$	$1.1x10^{-5}$	$0.94x10^{-5}$	$1.5x10^{-5}$	$0.2x10^{-5}$	$0.03x10^{-5}$	$0.01x10^{-5}$	$1.7x10^{-5}$
$8.0x10^4$	$0.88x10^{-5}$	$0.82x10^{-5}$	$1.2x10^{-5}$	$0.1x10^{-5}$	$0.03x10^{-5}$	negligible	$1.3x10^{-5}$
$9.0x10^4$	$0.68x10^{-5}$	$0.73x10^{-5}$	$1.0x10^{-5}$	$0.10x10^{-5}$	$0.02x10^{-5}$		$1.1x10^{-5}$
$10.0x10^4$	$0.56x10^{-5}$	$0.66x10^{-5}$	$0.87x10^{-5}$	$0.08x10^{-5}$	$0.02x10^{-5}$		$0.97x10^{-5}$

5. EXPERIMENTAL

5.1 Description of the Apparatus

A line diagram of the apparatus is shown in figure 5.1. The vacuum to the apparatus was provided by an "Edwards" two-stage rotary vacuum pump, model 2SC20A (1) and an "Edwards Speedivac" mercury vapour diffusion pump, model EM1 (4). Cold traps (3) and (5), immersed in liquid air, removed moisture, organic vapours and mercury from the system.

The mercury-in-glass manometer (6) was mounted on a rigid frame positioned between a fluorescent lamp and the cathetometer (23). The manometer was a U-tube manometer constructed of 20 mm bore tubing. A "Wild" model KM342 cathetometer was used to read the mercury levels in the manometer. This cathetometer, which measured the nitrogen pressure, had a one metre silica glass scale ruled in intervals of 0.1 mm to an accuracy of ±0.01 mm and could be read to within 0.02 mm or better.

The nitrogen gas which was used to nearly balance the cell sample gas pressure was drawn from a "New Zealand Industrial Gases Ltd" cylinder (8). This was connected to the apparatus, together with a mercury safety valve (9) to ensure that the pressure did not rise above one atmosphere. The nitrogen gas which was dried in a U-tube containing molecular sieve (10) passed into the apparatus through taps N2, N3 and N4. N3 was an "Edwards" fine-control needle valve, type OS1C, which allowed the nitrogen to be bled out slowly to ensure that the differential pressure transducer had a slightly greater pressure on the nitrogen side than on the cell side. This bleeding out process was accomplished by opening stopcock N1 to the vacuum system.

The degassing and loading manifold (11) could be isolated from the rest of the apparatus by stopcocks G4 and G5 which were oriented in such a way that the PTFE seals seated on the surface on the apparatus side of the stopcock. The sample ampoule (12) was connected to this manifold by a greased B10/19 "Quickfit" ground-glass vacuum cone and socket, while a "Young" stopcock (G6) was joined to the manifold so that the manifold could

be let down to atmosphere in order to release the ampoule for weighing.

The oil bath (13) of about 75 litres capacity contained "Shell Diala BX" transformer oil stirred by an impeller driven by a 185 W electric motor (19). The energy required to maintain the oil bath at a constant temperature was provided by two heaters. The first of these, a one kW immersion heater (14) whose voltage supply was controlled by a "Variac", provided about 85% of the required energy. The second heater was a "pyrotenax" heater surrounding the stirrer shaft which provided the remainder of the energy as required by the temperature controller. The S.C.R. temperature controller (Martin) was connected to the thermistor (16) immersed in the oil bath.

Partially immersed in the oil bath was a metal box (18) which had an asbestos lid. This was installed to house the metallic portion of the apparatus between the two glass cells so that if a leak developed in the metal joints then oil would not leak into the apparatus. To ensure that the inside of this container was at the same temperature as the oil bath, two fifteen watt pigmy lightbulbs in series with a "Variac" were installed. A mercury-in-glass thermometer was placed in this box to measure the temperature. The "Variac" was set so that the temperature of the contents of this box were the same as the oil bath. The metal tube between the Hoke valves H2 and H3 was stainless steel and out of this protruded a smaller diameter copper tube terminating in a "Cajon V.C.R." vacuum coupling gland and female nut. The other stubs of H2 and H3, as well as the two stubs on H1, were joined to copper tubes which were in turn joined to glass-to-metal seals. The female nut for the "Cajon" fitting was screwed to a "Cajon V.C.R." male connector, with an aluminium gasket placed between the connector and the gland, which was in turn screwed into the negative pressure port of the differential pressure cell (19). This differential pressure transducer was a "Pace" P7D±0.1 psi model transducer which was coupled to a "Pace" CD10 carrier demodulator. The output of ±10 volts d.c. was recorded on a "Toa" model EPR-2TC chart

recorder which was used on the range of full-scale deflection corresponding to 33.3 N m^{-2} pressure differential. The positive pressure port of the differential pressure transducer was connected through another "Cajon V.C.R." vacuum fitting to a copper tube to a glass-to-metal seal to the nitrogen side of the manometer and to the pressure jackets of the glass cells (20) and (21).

The sample gas containers (20) and (21) at the core of the apparatus, were constructed of glass by Mr F. Downing of the Chemistry Department. Since the analysis of the results did not require that the volumes of these cells be known exactly, they were made to approximately the same size of 1.5×10^{-3} m^3. A cold finger for liquid air extended into the inner portion of each of the double-walled cells to provide for the distillation of condensable material into them. The cells were double-walled with nitrogen gas being used inside the outer wall so that there would be no distortion caused by any pressure differential existing between the inner part and its surroundings.

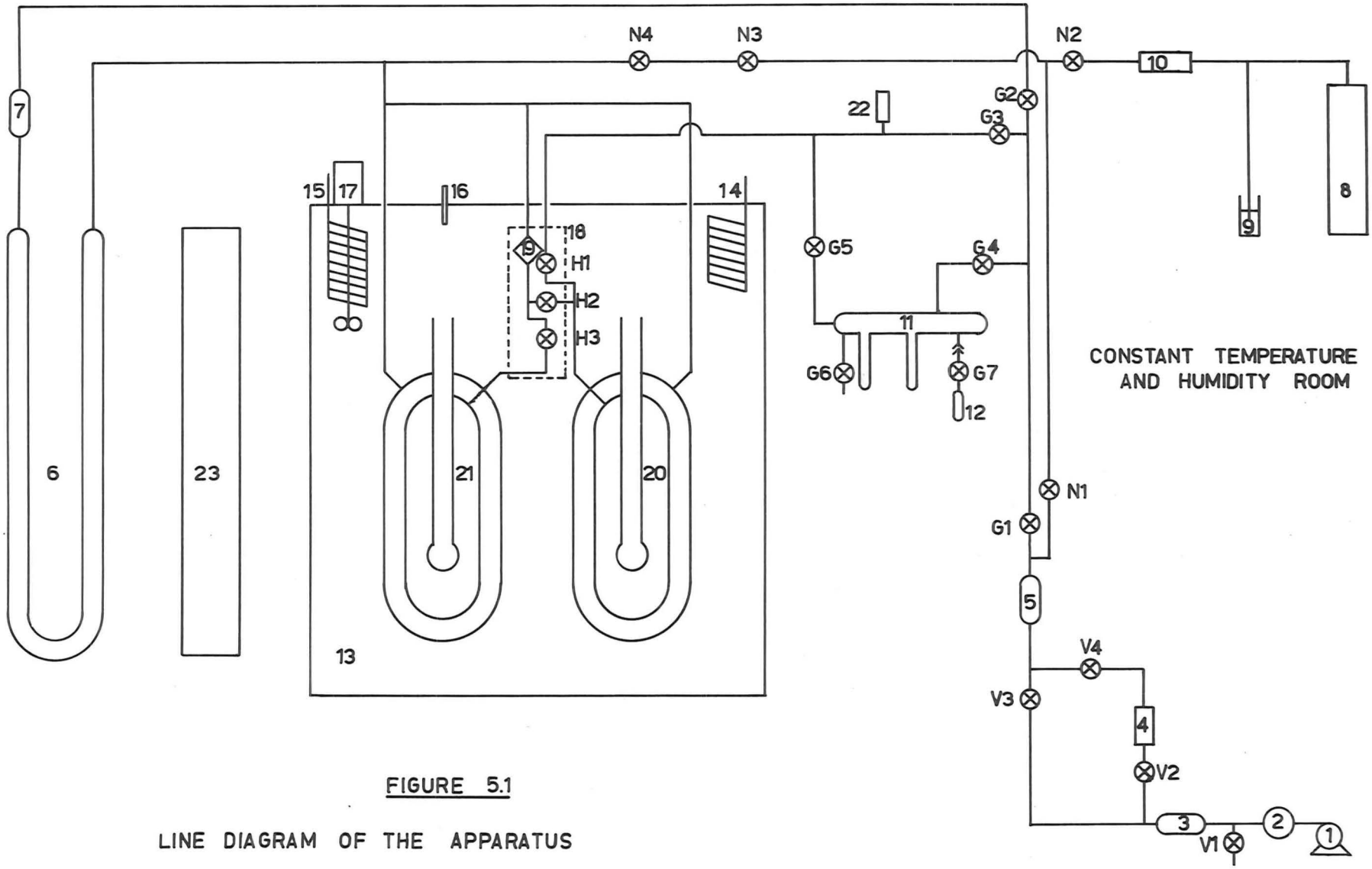


FIGURE 5.1

LINE DIAGRAM OF THE APPARATUS

Key to Figure 5.1

1. "Edwards" two-stage rotary vacuum pump, model 2SC20A.
2. 10^{-3} m^3 glass globe.
3. Liquid air cooled cold trap.
4. "Edwards Speedivac" mercury vapour diffusion vacuum pump with a 350 watt heater, model E.M.1.
5. Liquid air cooled cold trap.
6. Mercury-in-glass manometer.
7. Liquid air cooled cold trap.
8. Nitrogen gas supply bottle (N.Z. Industrial Gases Ltd).
9. Mercury safety valve to allow nitrogen to escape should the pressure exceed one atmosphere.
10. A U-tube containing molecular sieve to dry the nitrogen gas.
11. Degassing manifold with two distillation fingers and a B10/19 "Quickfit" socket for connecting the sample ampoule.
12. Sample ampoule with a B10/19 cone for attachment to the degassing manifold and a "Young" teflon/glass sealing tap.
13. Constant temperature oil bath of approximately 0.075 m^3 capacity containing "Shell Diala BX" transformer oil.
14. Main heater for the oil bath. Electric immersion 1 kW heater in series with a "Variac".
15. Intermittent "pyrotenax" heater connected to a S.C.R. temperature controller and a thermistor (16).
16. Thermistor for the oil bath temperature control.
17. A 185 W "Crompton Parkinson" electric motor attached to the oil bath stirrer.
18. A metal box with an asbestos top partially immersed in the oil bath. This box contained two 15 W pigmy lightbulbs, supplied through a "Variac", to ensure that the air inside was at the same temperature as the oil bath. Also housed in this box were the three "Hoke" valves, H1, H2 and H3, and the "Pace" differential pressure transducer (19).
19. "Pace" P7D±0.1 psi magnetic reluctance differential pressure transducer (connected to a "Pace" model CD10 carrier demodulator and a "Toa" model EPR-2TC chart recorder).
20. Glass double-walled cell of approximately 1.5×10^{-3} m^3 capacity. A cold finger for liquid air distillations extended to about two-thirds of the depth of the inner portion of the cell. The outer part of the cell, for the nitrogen equalising pressure, was about 1.5 cm from the inner part.
21. A glass cell similar to (20) and connected to it by glass-to-metal seals, a length of stainless steel tubing and two "Hoke" valves.
22. "Edwards Speedivac" Pirani vacuum gauge head, model G6B, connected to an "Edwards" model B5 gauge.
23. "Wild model KM342 cathetometer.

H1, H2 and H3 are "Hoke" all-metal diaphragm vacuum taps, 4600 series.

V1, V2, V3, V4, G1, G2, G3, N1, N2 and N3 are all ground-glass vacuum stopcocks.

G4, G5, G6 and G7 are "Young" high-vacuum stopcocks.

N3 is an "Edwards Speedivac" needle valve, type 0S1C.

The complete apparatus was housed in a constant humidity/constant temperature room.

5.2 Operating Procedure

The initial step with each experimental run was to evacuate the whole system. An indication of total vacuum, apart from the Pirani gauge, was the differential pressure transducer's recorder output. When the trace on this recorder was unchanging, the recorder itself was zeroed, after which the carrier demodulator zero was set so that a zero pressure differential corresponded to zero volts as shown by the recorder. At this point the nitrogen side of the system was isolated and a positive pressure, in excess of that anticipated for the first sample loading, was applied.

The "Hoke" valves H3 and H2 were shut, as were the stopcocks G3 and G4, to isolate the degassing and loading manifolds. Liquid air was then poured into the cold finger of cell I prior to opening the stopcock G7. After the desired amount of sample had evaporated from the sample ampoule, G7 was closed and an hour later when the Pirani gauge read, at the most, 0.3 N m^{-2} the "Hoke" valve H1 was shut. During this period it was ensured that adequate liquid air remained in the cold finger. Once H1 was shut the "Hoke" valve H2 was opened in preparation for the first pressure measurement. A thermometer was hung in the cold finger to give an indication as to when the contents of cell I (20) were at the oil bath temperature. While this was occurring the stopcock G5 was closed and G1 opened to allow the removal of the sample ampoule (12) which was weighed to determine the amount of sample loaded.

Generally up to three hours were allowed to elapse between the loading of a sample and the first pressure measurement. Over this period of time the nitrogen gas pressure was decreased to facilitate steady state being achieved. Care was taken to ensure that the nitrogen side of the pressure transducer was at a greater pressure than the sample side. With the recorder on the same range as used for the calibration of the differential pressure transducer, the nitrogen pressure was brought to about 25 N m^{-2} above that exerted by the sample gas. The pressure of the nitrogen was then read from the manometer after which the correction was made for the

pressure transducer offset from the null point. No correction was necessary for the expansion of the silica glass scale of the cathetometer.

Once the necessary readings for the pressure of the sample gas in cell I (20) had been obtained, the "Hoke" valve H3 was opened to allow the gas to expand into the whole apparatus and fill the second cell (21). After about an hour, during which time the nitrogen gas pressure was reduced to a point approaching the null point of the differential pressure transducer, the required pressure and temperature readings were taken.

At this juncture the nitrogen pressure was increased to a value in excess of that recorded for the sample when contained in cell I. A liquid air distillation was performed to transfer the sample across to cell II for which an hour was allowed. After this hour had elapsed, the "Hoke" valve H2 was closed to confine the sample to cell II. A similar procedure for measuring the pressure of the sample gas in cell II was carried out like the two previous measurements.

On completion of this step, another liquid air distillation was carried out, after opening H2, to transfer the sample back to cell I. After an hour had elapsed, H3 and H2 were shut. With the loading and degassing manifolds isolated the "Hoke" valve H1 was opened with any pressure rise, as shown by the Pirani gauge, being noted. Should there be no pressure rise an addition of some more sample gas to the amount already within the apparatus was made.

This whole procedure was repeated until four or five loadings, together with the associated pressure measurements, had been completed. The sample gas was then returned to the sample ampoule (12) with the aid of liquid air and the apparatus was evacuated to check for any zero shift of the differential pressure transducer.

The calibration of the offset for the "Pace" differential pressure transducer (19) was repeated at each temperature at which the experiment was carried out.

5.3 Calibration of the "Pace" P7D Variable Reluctance Pressure Transducer

The "Pace" P7D differential pressure transducer was calibrated by measuring a series of nitrogen gas pressures between 0.0 and 70.0 N m^{-2} applied to one side of the manometer. The other side of the pressure transducer and the vacuum side of the manometer were kept under a hard vacuum during this procedure. The nitrogen was adjusted through stopcocks N3 and N4 and when the manometer was read the corresponding milli-volt reading from the recorder was noted. The relation between the pressure differential and the carrier demodulator output as shown on the recorder was linear in the range of the calibration. The calibration factors at the temperatures used were as shown below.

Temperature	Calibration factor
328.15 K	66.6±2.0 N m^{-2} V^{-1}
343.15 K	66.6±2.0 N m^{-2} V^{-1}
358.15 K	66.6 ± 2.0 N m^{-2} V^{-1}
373.15 K	66.6±2.0 N m^{-2} V^{-1}

5.4 Calibration of the Common Volume

Although the method used in this work for determining second virial coefficients does not require the determination of the cell volumes, it does however need the evaluation of the small volume, ΔV, connecting the two cells to each other and the differential pressure transducer.

This volume was determined in two parts. The first was the differential pressure transducer together with the "Cajon" male connector. Into this small volume, toluene, whose density had been previously determined, was poured after the transducer had been weighed. After the addition of the toluene it was reweighed to determine the weight of toluene contained in the small volume in question. The second part was the piece comprising the "Hoke" valves H2 and H3 and the small diameter tube which terminated in the gland of the "Cajon" vacuum fitting. The

"Hoke" valves were oriented in such a way that the ΔV required was that between the two valves when they were both shut. By attaching a vacuum connection to the "Cajon" gland the assembly could be evacuated after which toluene was admitted under vacuum. By the weight difference of the assembly before and after the addition of the toluene the amount added could be found.

The weights of toluene needed to fill the valve assembly and the transducer could then be added and from the density of the toluene ΔV could be evaluated. This volume was $2.99 \pm 0.12 \times 10^{6}$ m^3.

5.5 Pressure Determination

The raw data for each loading of the apparatus comprised the weight of the sample and the three pressure readings to correspond to p_1, p_2 and p_3 as in equation 4.9.

Since the "Wild" cathetometer had a silica glass scale of very low coefficient of thermal expansion, no correction was necessary to compensate for temperature effects of the cathetometer scale.

The pressure of the sample gas within the apparatus was that of the nitrogen, as shown by the manometer, less the differential pressure transducer offset. The pressure of the nitrogen was determined using the following equation:

$$p/(N\ m^{-2}) = \rho^{Hg}_{t^oC} \times g_{local} \times \Delta H(mm\ Hg,\ t^oC) \times 0.01 \qquad (5.1)$$

The value of g_{local}, provided by the Christchurch Meteorological Service, was 980.48 cm s^{-2}. The variation in density of mercury with temperature as tabulated by Biggs (1964) was found to be described very well by the following equation obtained from the International Critical Tables (1927).

$$\rho(t) = \frac{13.59508}{1+1.81456\times10^{-4}(t) + 9.205\times10^{-9}(t)^2 + 6.608\times10^{-12}(t)^3 + 6.732\times10^{-14}(t)^4} \qquad (5.2)$$

This pressure in N m^{-2} was converted to a pressure in mmHg(0^oC) where

appropriate by the relation

$$p/(\text{mmHg}, 0^{\circ}\text{C}) = \frac{p/(\text{N m}^{-2})}{133.3224} \qquad (5.3)$$

5.6 Materials

The mercury for the manometer was purified and dried as described by Beath (1967).

Phillips Research Grade n-Hexane, lot number 1377, of guaranteed purity of 99.99 mole % was used.

The n-Hexane was thoroughly degassed by multiple distillations using liquid air as the coolant in the degassing manifold (item 11 in figure 5.1). Approximately five distillations were carried out and the manifold evacuated between each distillation while the fluid was held frozen with liquid air. For the final distillation the fluid was transferred to the sample ampoule (item 12 in figure 5.1).

6. EXPERIMENTAL RESULTS

6.1 Calculation Procedure for the Results

From equation 4.9

$$B' + C'(p_1 + p_2 - p_3) = RT\left(\frac{1}{p_3} - \frac{1}{p_1} - \frac{1}{p_2}\right) + \frac{\Delta V}{n} \qquad (6.1)$$

$$= B'_{apparent}$$

By plotting $B'_{apparent}$ against $(p_1 + p_2 - p_3)$ we obtain B' as the intercept,

$$B' = \lim_{(p_1+p_2-p_3)\to 0} B'_{apparent} \qquad (6.2)$$

This determines a pressure series second virial coefficient at temperature T for the substance under investigation.

If the volume series equation:

$$p = \left(\frac{n}{V}\right)RT + \left(\frac{n}{V}\right)^2 BRT \qquad (6.3)$$

is used, then for each case: all of the sample in the first cell, all in the second cell and, thirdly, shared between both cells, a volume series virial equation may be written. A second virial coefficient may be found from the resulting three equations using the iterative technique described in section 4.2. The second virial coefficients obtained using this method, when plotted against $(p_1 + p_2 - p_3)$, should produce a line that intersects the y-axis at the same point as the line obtained from a graph of $B'_{apparent}$ versus $(p_1 + p_2 - p_3)$ since from equation 4.16

$$B' = B.$$

Straight lines, deduced by the method of least squares, are drawn through the two sets of points to determine B' and B as described in appendix 1.

6.2 Results

6.2.1 Results at 328.15 K

6.2.1.1 Raw Results

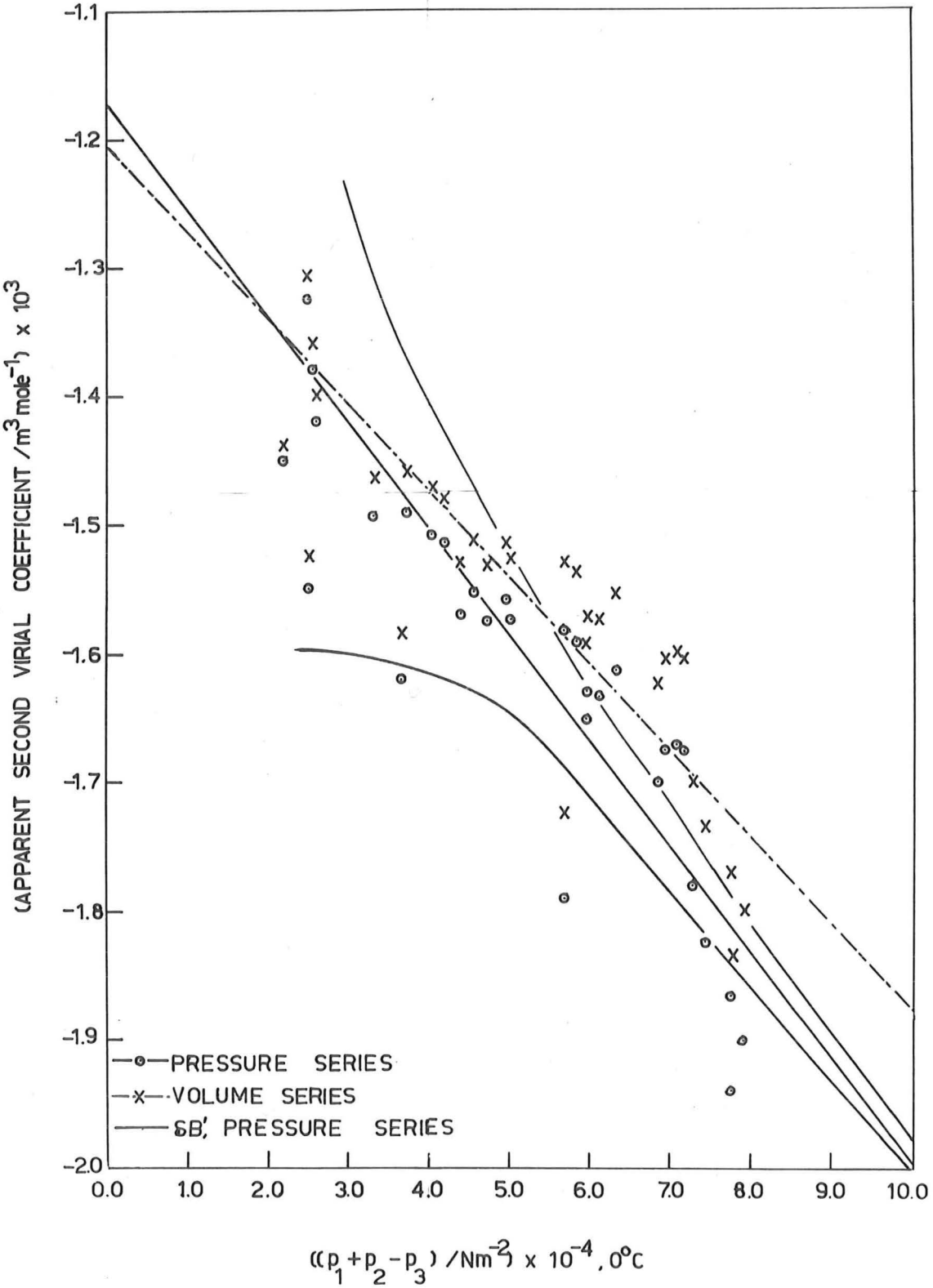
$(p_1/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(p_2/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(p_3/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(\Delta V/n)/m^3\ mole^{-1})$ $x10^4$
1.4565	1.4715	0.7356	3.521
1.6541	1.6714	0.8355	3.097
1.6813	1.6987	0.8499	3.060
1.7163	1.7343	0.8673	2.985
1.7253	1.7435	0.8719	2.968
2.2172	2.2401	1.1222	2.304
2.4310	2.4558	1.2318	2.098
2.4779	2.5026	1.2548	2.058
2.6974	2.7228	1.3666	1.890
2.8031	2.8318	1.4211	1.816
2.9202	2.9490	1.4812	1.743
3.0389	3.0692	1.5419	1.674
3.1495	3.1804	1.5985	1.614
3.2881	3.3215	1.6696	1.544
3.3397	3.3720	1.6959	1.520
3.7780	3.8137	1.9208	1.341
3.7861	3.8344	1.9309	1.333
3.9083	3.9474	1.9885	1.295
3.9615	3.9973	2.0158	1.277
3.9738	4.0115	2.0224	1.273
4.0795	4.1170	2.0765	1.239
4.2213	4.2605	2.1493	1.196
4.5587	4.5986	2.3245	1.106
4.6275	4.6679	2.3597	1.089
4.7135	4.7569	2.4046	1.068
4.7884	4.8295	2.4427	1.051
4.8720	4.9101	2.4875	1.032
4.9804	5.0172	2.5442	1.009
5.1888	5.2265	2.6535	0.966
5.2004	5.2400	2.6619	0.964
5.2825	5.3224	2.7036	0.949

6.2.1.2 Calculated Results

$((p_1+p_2-p_3)/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(B'_{apparent}/m^3\ mole^{-1})$ $x10^3$	$(B_{apparent}/m^3\ mole^{-1})$ $x10^3$
2.1924	-1.451	-1.440
2.4900	-1.326	-1.308
2.5301	-1.549	-1.524
2.5833	-1.381	-1.360
2.5969	-1.420	-1.400
3.3351	-1.493	-1.464
3.6550	-1.619	-1.584
3.7257	-1.491	-1.460
4.0536	-1.507	-1.472
4.2138	-1.513	-1.479
4.3880	-1.569	-1.530
4.5662	-1.552	-1.512
4.7314	-1.575	-1.532
4.9400	-1.558	-1.515
5.0158	-1.573	-1.528
5.6709	-1.582	-1.531
5.6896	-1.789	-1.724
5.8672	-1.591	-1.538
5.9430	-1.651	-1.592
5.9629	-1.629	-1.572
6.1200	-1.634	-1.576
6.3325	-1.613	-1.554
6.8328	-1.697	-1.626
6.9357	-1.674	-1.604
7.0658	-1.670	-1.599
7.1752	-1.676	-1.604
7.2946	-1.780	-1.697
7.4534	-1.823	-1.734
7.7618	-1.866	-1.770
7.7785	-1.940	-1.835
7.9013	-1.902	-1.799

FIGURE 6.1

APPARENT SECOND VIRIAL COEFFICIENT VERSUS $(p_1+p_2-p_3)$ AT 328.15 K



Regression coefficients were derived, as detailed in Appendix 1, from a plot of the results at 328.15 K, figure 6.1, in the form

$Y = a + bx$ where:

Y is the apparent second virial coefficient, and

x is the pressure term $(p_1 + p_2 - p_3)$.

Pressure series:

$a = -117.3 \times 10^{-5}$ m^3 $mole^{-1}$ Standard error = 2.4×10^{-5} m^3 $mole^{-1}$

$b = -830 \times 10^{-11}$ m^5 $mole^{-1}$ N^{-1} Standard error = 44×10^{-11} m^5 $mole^{-1}$ N^{-1}

Volume series:

$a = -120.4 \times 10^{-5}$ m^3 $mole^{-1}$ Standard error = 2.2×10^{-5} m^3 $mole^{-1}$

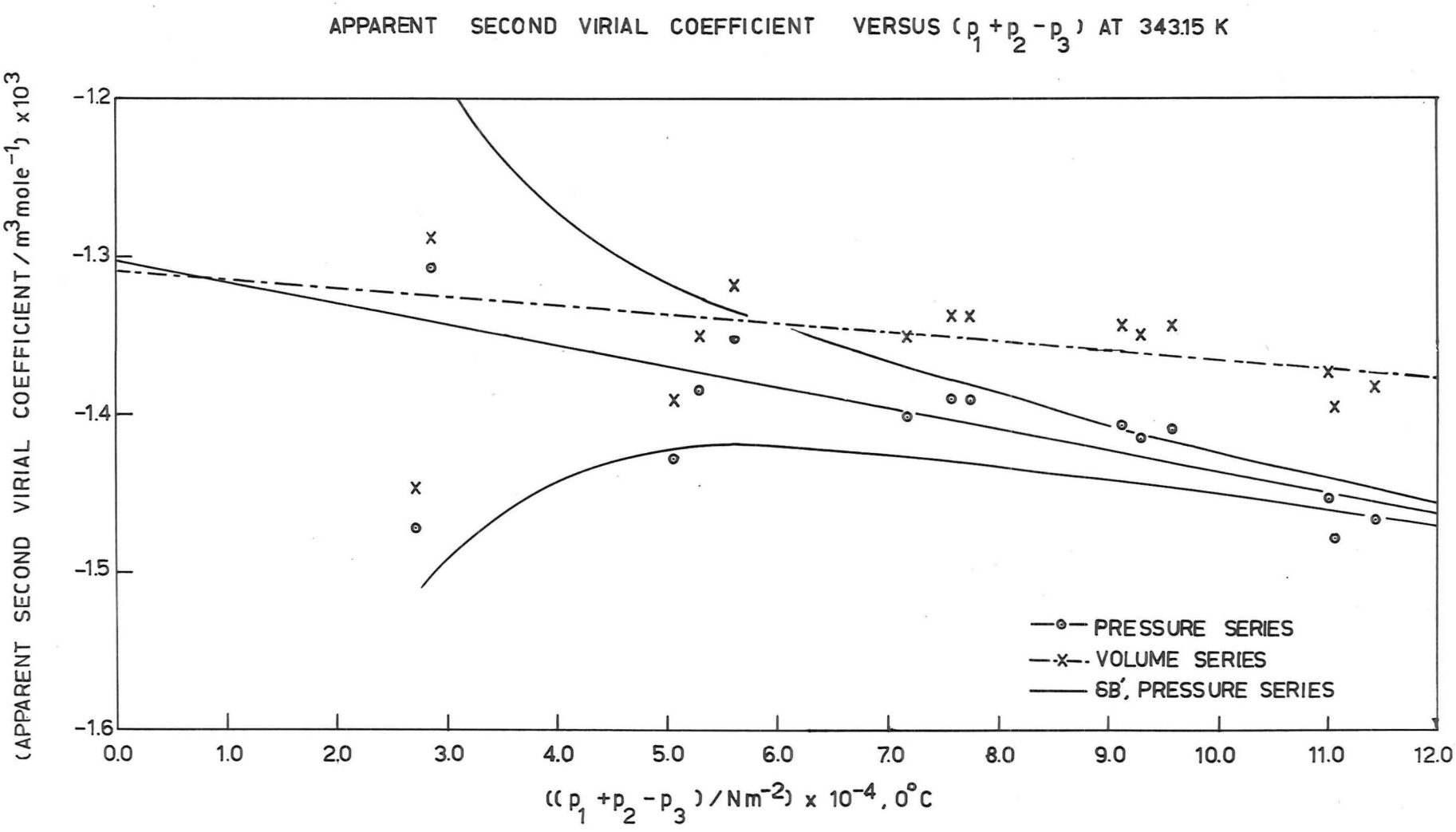
$b = -674 \times 10^{-11}$ m^5 $mole^{-1}$ N^{-1} Standard error = 39×10^{-11} m^5 $mole^{-1}$ N^{-1}

6.2.2 Results at 343.15 K

6.2.2.1 Raw Results

$(p_1/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(p_2/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(p_3/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(\Delta V/n)/m^3\ mole^{-1})$ $x10^4$
1.8073	1.8264	0.9135	2.971
1.8928	1.9128	0.9565	2.835
3.3592	3.3967	1.7049	1.584
3.5096	3.5466	1.7809	1.518
3.7205	3.7586	1.8882	1.430
4.7731	4.8209	2.4293	1.109
5.0473	5.0969	2.5702	1.048
5.1633	5.2154	2.6303	1.024
6.0836	6.1435	3.1064	0.864
6.1999	6.2595	3.1667	0.848
6.3864	6.4493	3.2637	0.822
7.3463	7.4161	3.7648	0.711
7.3874	7.4626	3.7888	0.707
7.6286	7.7002	3.9127	0.684

FIGURE 6.2


APPARENT SECOND VIRIAL COEFFICIENT VERSUS (p1 + p2 - p3) AT 343.15 K
(APPARENT SECOND VIRIAL COEFFICIENT / m3 mole-1) x 10^3
-1.2
-1.3
-1.4
-1.5
-1.6
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
((p1 + p2 - p3) / Nm-2) x 10-4 , 0°C
PRESSURE SERIES
VOLUME SERIES
6B', PRESSURE SERIES

6.2.2.2 Calculated Results

$((p_1+p_2-p_3)/N\ m^{-2})$ $x10^{-4}$, $0^{o}C$	$(B'_{apparent}/m^3\ mole^{-1})$ $x10^3$	$(B_{apparent}/m^3\ mole^{-1})$ $x10^3$
2.7202	-1.472	-1.448
2.8491	-1.307	-1.288
5.0510	-1.429	-1.392
5.2753	-1.385	-1.351
5.5909	-1.353	-1.318
7.1647	-1.401	-1.352
7.5740	-1.390	-1.339
7.7484	-1.391	-1.339
9.1207	-1.407	-1.345
9.2927	-1.415	-1.351
9.5720	-1.410	-1.345
10.9976	-1.454	-1.374
11.0612	-1.479	-1.396
11.4161	-1.467	-1.383

Regression coefficients were derived as detailed in Appendix 1, from a plot of the results at 343.15 K, figure 6.2, in the form Y = a + bx, where:

Y is the apparent second virial coefficient, and

x is the pressure term $(p_1 + p_2 - p_3)$.

Pressure series:

$a = -130.2x10^{-5}\ m^3\ mole^{-1}$ Standard error = $0.9x10^{-5}\ m^3\ mole^{-1}$

$b = -137x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$ Standard error = $11x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$

Volume series:

$a = -130.9x10^{-5}\ m^3\ mole^{-1}$ Standard error = $0.8x10^{-5}\ m^3\ mole^{-1}$

$b = -57x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$ Standard error = $10x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$

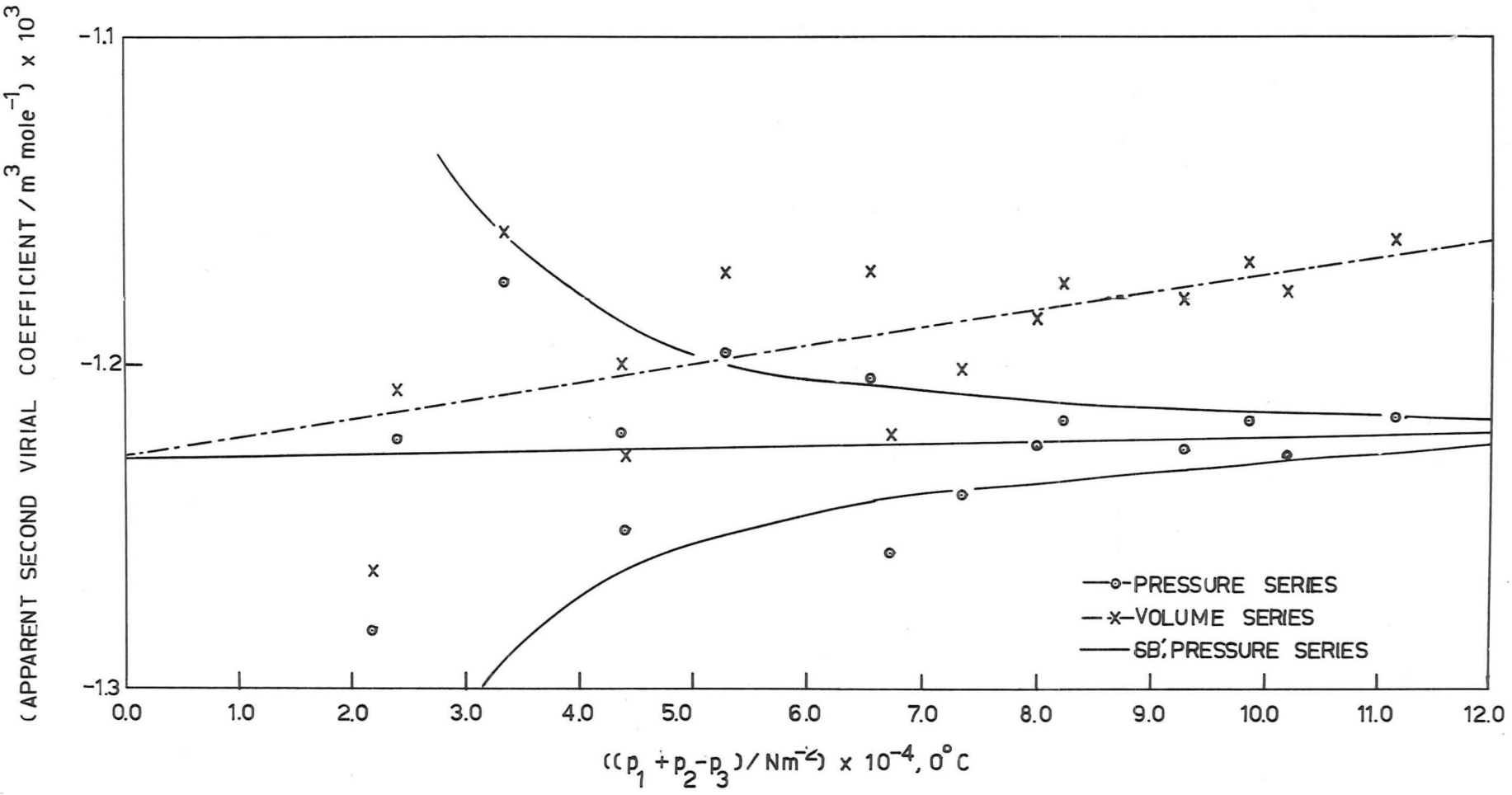
6.2.3 Results at 358.15 K

6.2.3.1 Raw Results

$(p_1/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(p_2/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(p_3/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(\Delta V/n)/(m^3\ mole^{-1})$ $x10^4$
1.4329	1.4485	0.7233	3.926
1.5948	1.6117	0.8050	3.518
2.2212	2.2454	1.1226	2.523
2.9094	2.9398	1.4724	1.922
2.9236	2.9544	1.4800	1.910
3.5100	3.5474	1.7785	1.588
4.3463	4.3915	2.2060	1.278
4.4940	4.5404	2.2825	1.236
4.8837	4.9352	2.4823	1.135
5.2998	5.3553	2.6958	1.045
5.4442	5.5007	2.7696	1.015
6.1802	6.2452	3.1495	0.892
6.5760	6.6440	3.3533	0.837
6.7984	6.8685	3.4688	0.809
7.4386	7.5161	3.8001	0.737

FIGURE 6.3

APPARENT SECOND VIRIAL COEFFICIENT VERSUS $(p_1 + p_2 - p_3)$ AT 358.15 K



6.2.3.2 Calculated Results

$((p_1+p_2-p_3)/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(B'_{apparent}/m^3\ mole^{-1})$ $x10^3$	$(B_{apparent}/m^3\ mole^{-1})$ $x10^3$
2.1581	-1.282	-1.264
2.4015	-1.223	-1.208
3.3440	-1.175	-1.160
4.3768	-1.221	-1.200
4.3980	-1.251	-1.228
5.2789	-1.196	-1.172
6.5318	-1.204	-1.172
6.7519	-1.258	-1.222
7.3366	-1.240	-1.202
7.9593	-1.225	-1.186
8.1753	-1.217	-1.176
9.2759	-1.226	-1.180
9.8667	-1.217	-1.169
10.1981	-1.228	-1.178
11.1546	-1.216	-1.162

Regression coefficients were derived, as detailed in Appendix 1, from a plot of the results at 358.15 K, figure 6.3, in the form

$Y = a + bx$, where:

Y is the apparent second virial coefficient, and

x is the pressure term $(p_1 + p_2 - p_3)$.

Pressure series:

$a = -122.9x10^{-5}\ m^3\ mole^{-1}$ Standard error = $0.4 \times 10^{-5}\ m^3\ mole^{-1}$

$b = 8x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$ Standard error = $6x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$

Volume series:

$a = -122.8x10^{-5}\ m^3\ mole^{-1}$ Standard error = $0.4x10^{-5}\ m^3\ mole^{-1}$

$b = 55x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$ Standard error = $5x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$

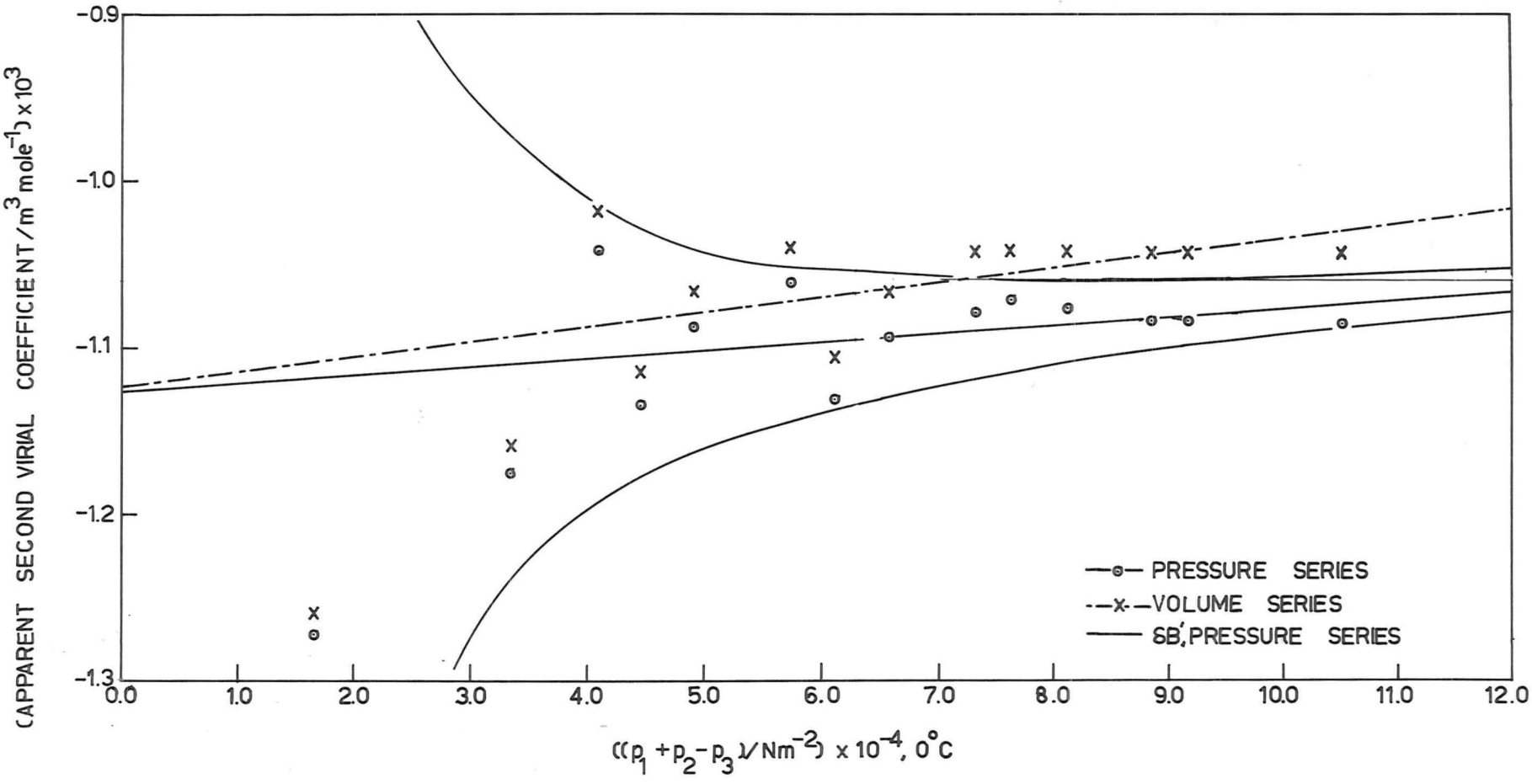
6.2.4 Results at 373.15 K

6.2.4.1 Raw Results

$(p_1/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(p_2/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(p_3/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(\Delta V/n)/(m^3\ mole^{-1})$ $x10^4$
1.0931	1.1055	0.5514	5.376
2.2248	2.2490	1.1242	2.631
2.7232	2.7532	1.3767	2.142
2.9698	3.0014	1.5024	1.964
3.2592	3.2943	1.6493	1.789
3.8082	3.8508	1.9292	1.526
4.0752	4.1189	2.0658	1.425
4.3666	4.4136	2.2142	1.330
4.8624	4.9151	2.4677	1.191
5.0820	5.1376	2.5801	1.139
5.4241	5.4824	2.7552	1.067
5.8858	5.9480	2.9920	0.981
6.1016	6.1678	3.1035	0.945
6.9992	7.0732	3.5652	0.822

FIGURE 6.4

APPARENT SECOND VIRIAL COEFFICIENT VERSUS $(p_1 + p_2 - p_3)$ AT 373.15 K



6.2.4.2 Calculated Results

$((p_1+p_2-p_3)/N\ m^{-2})$ $x10^{-4}$, 0^oC	$(B'_{apparent}/m^3\ mole^{-1})$ $x10^3$	$(B_{apparent}/m^3\ mole^{-1})$ $x10^3$
1.6472	-1.272	-1.260
3.3496	-1.176	-1.160
4.0997	-1.046	-1.020
4.4688	-1.135	-1.116
4.9042	-1.088	-1.068
5.7298	-1.062	-1.042
6.1281	-1.132	-1.107
6.5660	-1.094	-1.068
7.3098	-1.079	-1.044
7.6395	-1.071	-1.043
8.1513	-1.076	-1.044
8.8418	-1.084	-1.044
9.1659	-1.084	-1.044
10.5072	-1.085	-1.044

Regression coefficients were derived, as detailed in Appendix 1, from a plot of the results at 373.15 K, figure 6.4, in the form

Y = a + bx, where:

Y is the apparent second virial coefficient, and

x is the pressure term $(p_1 + p_2 - p_3)$.

Pressure series:

$a = -112.7x10^{-5}\ m^3\ mole^{-1}$ Standard error = $0.6x10^{-5}\ m^3\ mole^{-1}$

$b = 50x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$ Standard error = $10x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$

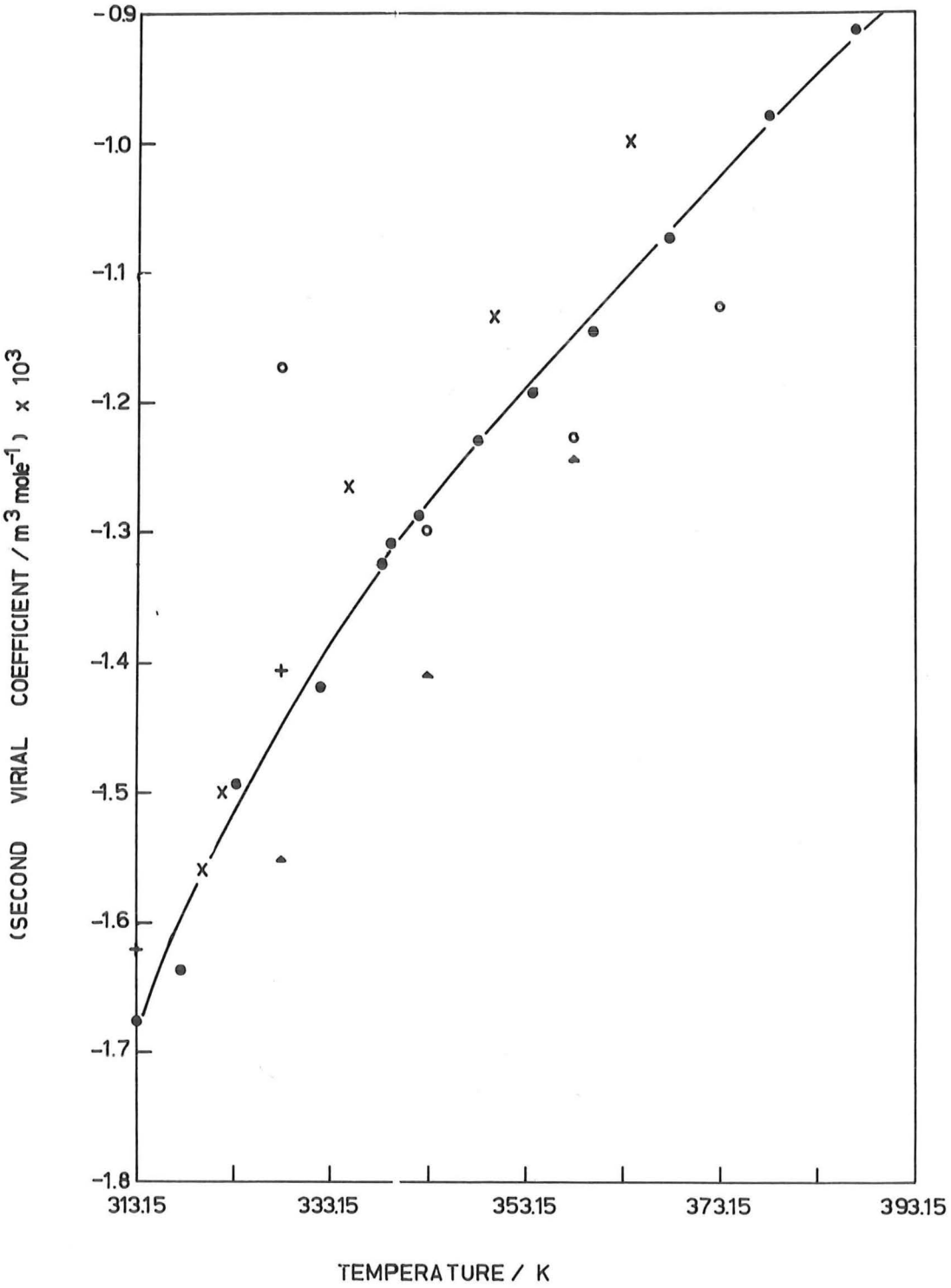
Volume series:

$a = -112.4x10^{-5}\ m^3\ mole^{-1}$ Standard error = $0.6x10^{-5}\ m^3\ mole^{-1}$

$b = 89x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$ Standard error = $10x10^{-11}\ m^5\ mole^{-1}\ N^{-1}$

FIGURE 6.5

SECOND VIRIAL COEFFICIENT OF n-HEXANE VERSUS TEMPERATURE



- o THIS WORK
- ● McGLASHAN AND POTTER
- \+ BOTTOMLEY AND REEVES
- x LAMBERT, ROBERTS, ROWLINSON AND WILKINSON
- ▲ PANDYA

FIGURE 7.1

VIRIAL COEFFICIENTS OF N-HEXANE

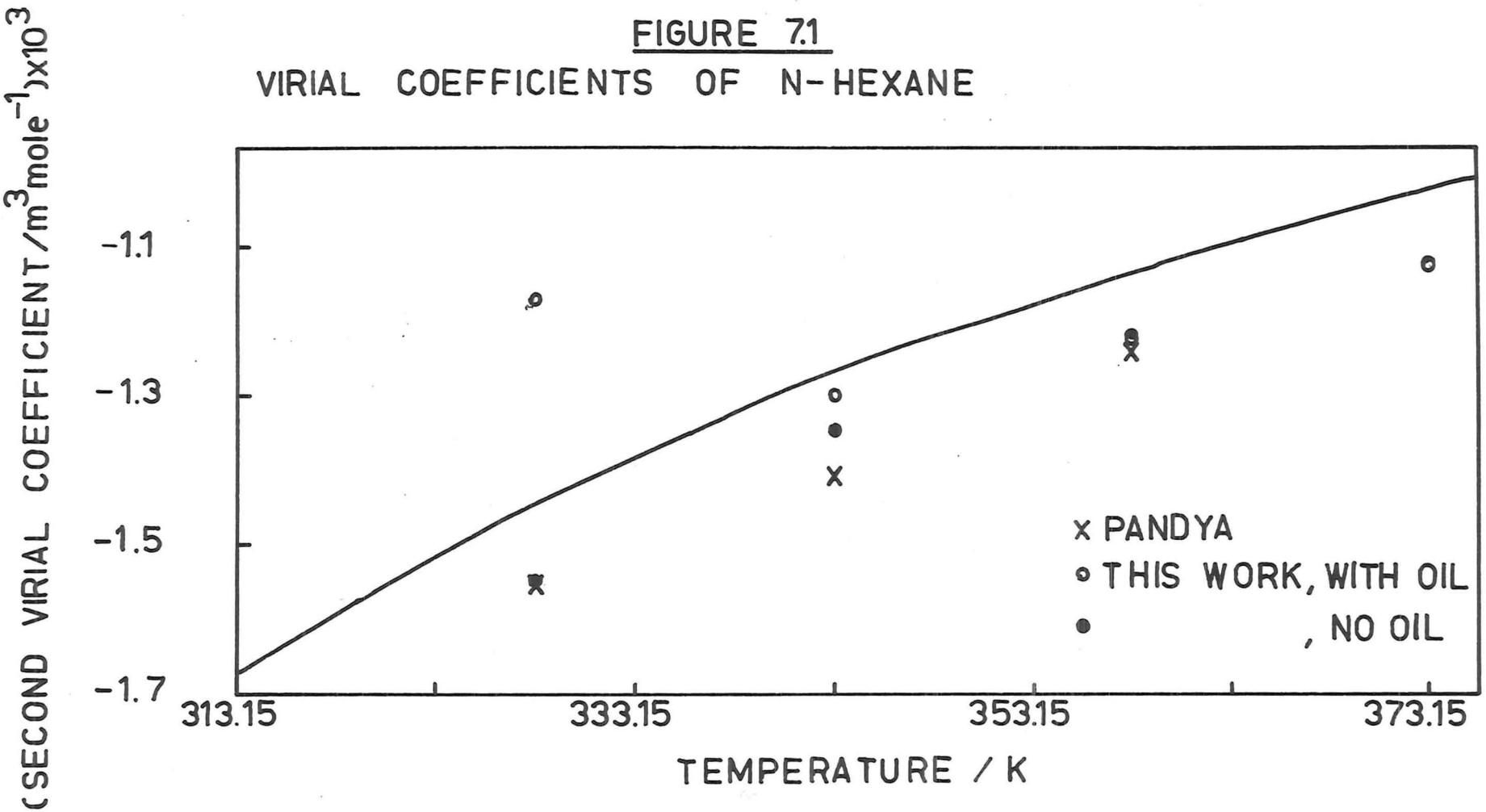
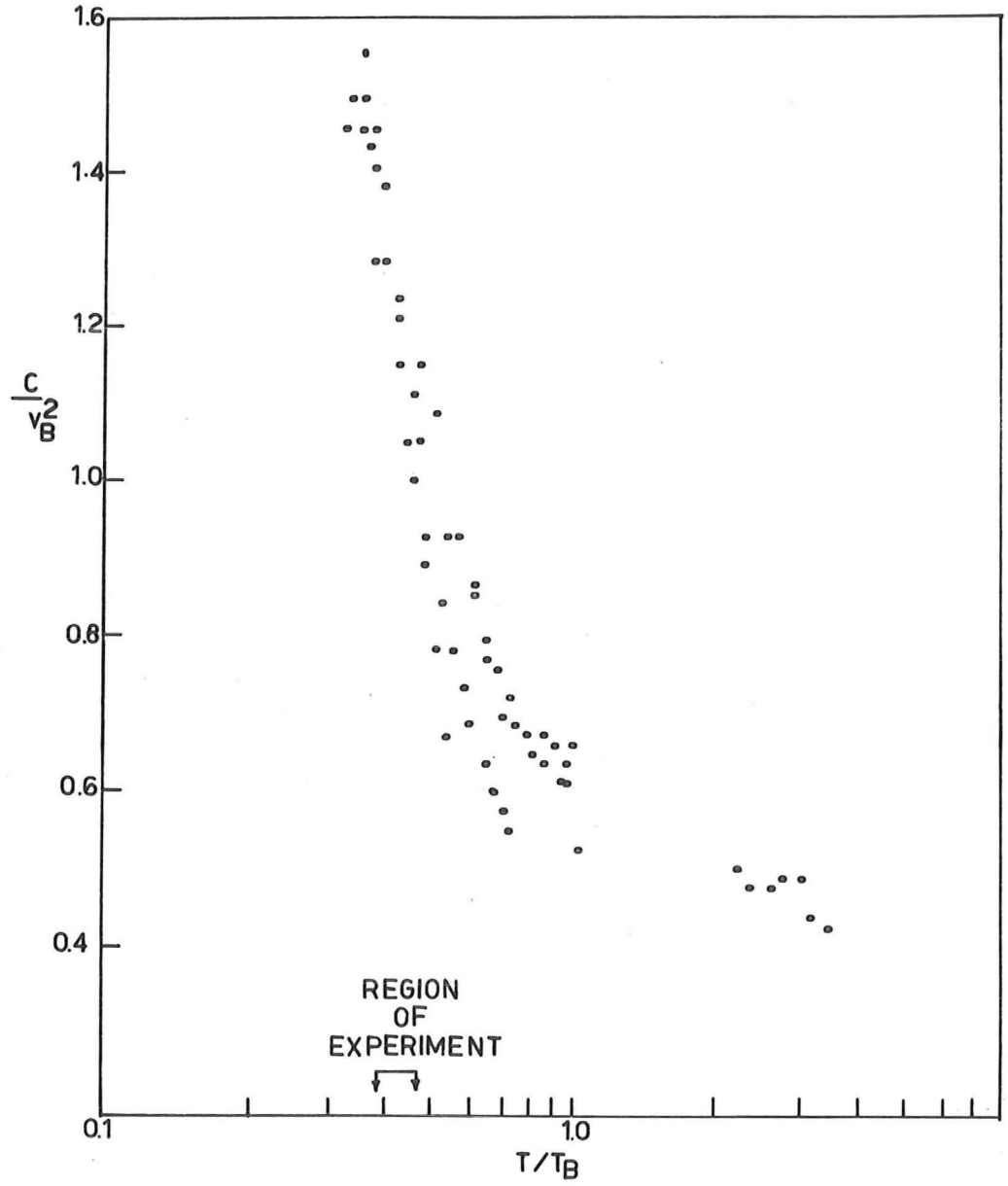


FIGURE 7.2

REDUCED THIRD VIRIAL COEFFICIENTS VERSUS REDUCED TEMPERATURE



C = THIRD VIRIAL COEFFICIENT
B = SECOND VIRIAL COEFFICIENT
T_B = BOYLE TEMPERATURE

$$v_B = T\left(\frac{dB}{dT}\right)_{T=T_B}$$

T = TEMPERATURE

7. CONCLUSION

The results given in this thesis for the second virial coefficients of n-Hexane are at variance with those reported in the literature, Dymond and Smith (1969), as shown in figure 6.5.

Early in the course of this work part of the apparatus collapsed under the surface of the oil bath with the result that oil filled part of it. Every effort was made to clean the oil completely from the apparatus but it is suspected that after the repairs and modifications were completed a trace of oil remained. In Appendix 9.2 the effect of a small amount of oil is examined. At lower pressures the effect of the oil on the value of $B'_{apparent}$ will be less than that at higher pressures. As the temperature increases there is less tendency for some of the gas to be dissolved in the oil with the result that this effect becomes less as the temperature increases. It would not be unreasonable to draw a curve through the values of $B'_{apparent}$ at 328.15 K, figure 6.1, and this could reasonably be explained by the presence of a small trace of oil within one cell of the apparatus. This curve would intercept the y-axis at a value of $B'_{apparent}$ more negative than the weighted least squares line drawn. By assuming that 1.4×10^{-4} moles of oil exist in one cell of the apparatus the value of B' for this work can be made to coincide with Pandya's value at 328.15 K using the procedure outlined in Appendix 9.2. This amount of oil does not bring the value at 343.15 K for this work down to that of the Pandya work but to within 60×10^{-6} m^3 $mole^{-1}$. At 358.15 K all three points, as shown in figure 7.1, are within 45×10^{-6} m^3 $mole^{-1}$ of each other. At 373.15 K, although there is no Pandya data to compare with, the result continues the trend of being about 90×10^{-6} m^3 $mole^{-1}$ below the literature values. As shown in figure 7.1, the effect of a small amount of oil within one cell of the apparatus is not great at this temperature.

From graphs of experimental points in Mason and Spurling (1969) and shown in figure 7.2, it is noted that the third virial coefficient increases as the temperature decreases. Although the experimental values of C',

obtained from the results in this work, show the opposite trend those values that arise from assuming the existence of a small trace of oil do follow the trend observed in figure 7.2. These values are noted in Appendix 9.2 and although not carrying as much weight as the values of B' confirm the presence of oil within the apparatus.

It is further suggested that if the apparatus were oil-free, then a curve through the results obtained using this method would lie consistently about 90×10^{-6} m^3 $mole^{-1}$ below the literature plot. In the past a great deal of virial coefficient data has been obtained by plotting pV versus p or v and extrapolating to zero pressure or density respectively. As Scott and Dunlap (1962) point out, the virial coefficients should be the limiting slopes of these plots rather than the average slopes. By extrapolating and using the average slope for a second virial coefficient previous workers are assuming that the third virial coefficient is zero. Scott and Dunlap further point out that by truncating both the density series and pressure series equations at the term in the second virial coefficient then different values are obtained for B and B' respectively. However by truncation of these equations at the third virial coefficient and fitting the experimental data to a least squares quadratic equation in v or p, then the values of B and B' were almost identical and rather different from those obtained previously by truncation of the virial equations at the second virial coefficient. It is suggested that the difference between the extrapolated virial coefficients in this work and the literature values result from the truncation and plotting methods used in the previous work and that employed here. The coincidence of the y-axis intercepts at higher temperatures from both the pressure series and the density series virial equations gives added weight to the assertions made here.

Since the scatter of the experimental points is to a large extent due to errors introduced in the pressure measurements, it would be desirable to use a more accurate pressure measuring device.

A check on the zero of the differential pressure transducer would be an added advantage. Hall and Eubank (1974) have used an arrangement of a Burnett apparatus where they could check their differential pressure transducer during the course of an experiment without greatly upsetting the run.

The problems associated with the scrupulous cleaning of the apparatus that is necessary can to a large extent be overcome by building from materials that can be baked to high temperatures and either vaporising or carbonising the traces of any unwanted material.

8. REFERENCES

Abraham, W.H., Bennett, C.O., A.I.Ch.E.J., 1960, 6, 257

Alexander, E.A., Lambert, J.D., Trans. Faraday Soc., 1941, 37, 421

Anderson, L.N., Kudchadker, A.P., Eubank, J. Chem. Eng. Data, 1968, 13, 321

Andon, R.J.L., Cox, J.D., Herington, E.F.G., Martin, J.F., Trans. Faraday Soc., 1957, 53, 1074

Ashton, J.G., Finke, H.L., Bestul, A.B., Pace, E.L., Szasz, G.J., J. Am. Chem. Soc., 1946, 68, 52

Bartels, R., Eucken, A., Z. Phys. Chem., 1921, 98, 70

Barton, J.R., Hsu, C.C., J. Chem. Eng. Data, 1969, 14, 184

Beath, L.A., Ph.D. Thesis, University of Otago, 1967

Benedict, M.J., J. Am. Chem. Soc., 1937, 59, 2224

Biggs, P.H., Brit. J. Appl. Phys., 1964, 15, 1111

Bloomer, O.T., Inst. Gas Tech. Research Bulletin, 1952, 13

Bottomley, G.A., Aust. J. Chem., 1960, 13, 311

Bottomley, G.A., Reeves, C.G., J. Chem. Soc., 1958, 161, 3794

Bottomley, G.A., Reeves, C.G., Whytlaw-Gray, R., Proc. Roy. Soc., 1958, A246, 504

Bottomley, G.A., Spurling, T.H., Aust. J. Chem., 1964, 17, 501

Bridgman, P.W., The Physics of High Pressure, London, Bell, 1949

Burnett, E.S., Phys. Rev., 1923, 22, 590

Burnett, E.S., J. Appl. Mechanics, 1936, 3, A136

Casado, F.L., Massie, D.S., Whytlaw-Gray, R., Proc. Roy. Soc., 1951, A207, 483

Cawood, W., Patterson, H.S., J. Chem. Soc., 1932, 135, 2180

Charnley, A., Isles, G.L., Townley, J.R., Proc. Roy. Soc., 1953, A218, 133

Cherney, B.J., Marchman, H., York, R., Ind. Eng. Chem., 1949, 41, 2653

Christchurch Meteorological Service, personal communication

Connolly, J.F., Kandalic, G.A., Phys. Fluids, 1960, 3, 463

Cottrell, T.L., Hamilton, R.A., Trans. Faraday Soc., 1956, 52, 156

Cox, J.D., Andon, R.J.L., Trans. Faraday Soc., 1958, 54, 1622

Cox, J.D., Lawrenson, J.J., Chemical Thermodynamics, Vol. 1, London, John Wright and Sons, 1973

Cruickshank, A.J.B., Windsor, M.L., Young, C.L., Proc. Roy. Soc., 1966, A295, 259

David, H.G., Hamann, S.D., Trans. Faraday Soc., 1953, 49, 711

Davies, O.L. (Ed.), Statistical Methods in Research and Production, 3rd edition, London, Oliver and Boyd, 1967

Day, H.O., Felsing, W.A., J. AM. Chem. Soc., 1952, 74, 1951

Dymond, J.H., Smith, E.B., The Virial Coefficients of Gases, Oxford, Clarendon Press, 1969

Edwards J.D., Ind. Eng. Chem., 1917, 9, 790

Edwards, A.E., Roseveare, W.E., J. Am. Chem. Soc., 1942, 64, 2816

Eon, C., Pommier, C., Guiorchon, G., J. Chem. Eng. Data, 1971, 16, 408

Eubank, P.T., Kerns, W.J., A.I.Ch.E.J., 1973, 19, 711

Everett, D.H., Stoddart, C.T.H., Trans. Faraday Soc., 1961, 57, 746

Francis, P.G., McGlashan, M.L., Wormald, C.J., J. Chem. Thermo., 1969, 1, 441

Giauque, W.F., Buffington, R.M., Schulze, W.A., J. Am. Chem. Soc., 1927, 49, 2343

Grimsrud, D.J., Werntz, J.H., Phys. Rev., 1967, 157, 181

Guye, P.A., Batuecas, T.J., J. Chim. Phys., 1923, 20, 308

Hajjar, R.F., Kay, W.B., Leverett, G.F., J. Chem. Eng. Data, 1969, 14, 377

Hajjar, R.F., MacWood, G.E., J. Chem. Phys., 1968, 49, 4567

Hall, K.R., Eubank, P.T., A.I.Ch.E.J., 1974, 20, 815

Hamann, S.D., McManamey, W.J., Trans. Faraday Soc., 1953, 49, 149

Hamann, S.D., Pearse, J.F., Trans. Faraday Soc., 1952, 48, 101

Haworth, W.S., Sutton, L.E., J. Phys. (E)., 1970, 3, 271

Hewlett-Packard Calculator Model 9100A Program Library, Part No. 09100-70811, Dec. 1968

Hill, T.L., Introduction to Statistical Thermodynamics, Reading, Addison-Wesley, 1962

Hirth, L.J., Kobe, K.A., J. Chem. Eng. Data, 1961, 6, 229

Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., Molecular Theory of Gases and Liquids, New York, Wiley, 1954

Hou, Y.C., Martin, J.J., A.I.Ch.E.J., 1959, 5, 125

International Critical Tables, Vol. II, New York, McGraw-Hill, 1927, p 457

Johnson, H.L., J. Am. Chem. Soc., 1946, 68, 2362

Johnson, H.L., Weimar, H.R., J. Am. Chem. Soc., 1934, 56, 625

Kappallo, W., Lund, N., Schäfer, K., Z. Phys. Chem., 1963, 37, 196

Kell, G.S., McLaurin, G.E., J. Chem. Phys., 1969, 51, 4345

Kell, G.S., Whalley, E., Trans. Faraday Soc., 1965, A258, 565

Keller, W.E., Phys. Rev., 1955, 97, 1

King, R.C., Potter, J.H., Trans. A.S.M.E., Series B., 1962, 84, 180

Kistemaker, J., Keesom, W.H., Physica, 1946, 12, 227

Knobler, C.M., Beenakker, J.J.M., Knaap, H.F.P., Physica, 1959, 25, 909

Knoebel, D.H., Edmister, W.C., J. Chem. Eng. Data, 1968, 13, 312

Kretschmer, C.B., Wiebe, R.J., J. Am. Chem. Soc., 1951, 73, 3778

Lambert, J.D., Clarke, J.S., Duke, J.F., Hicks, C.L., Lawrence, S.D., Morris, D.M., Shone, M.G.T., Proc. Roy. Soc., 1959, A249, 414

Lambert, J.D., Roberts, G.A.H., Rowlinson, J.S., Wilkinson, V.J., Proc. Roy. Soc., 1949, A196, 113

Lipsicas, M., Bloom, M., Muller, J. Chem. Phys., 1961, 34, 1813

Long, E.A., Gulbransen, E.A., J. Am. Chem. Soc., 1936, 58, 203

Martin, M.L., University of Adelaide, personal communication

Mason, E.A., Spurling, T.H., The Virial Equation of State, Oxford, Pergamon Press, 1969

McCullough, J.D., Scott, D.W., Finke, H.L., Gross, M.E., Williamson, K.D., Pennington, R.E., Waddington, G., Huffman, H.M., J. Am. Chem. Soc., 1952, 74, 2801

McCullough, J.P., Scott, D.W., Pennington, R.E., Hossenlopp, I.A., Waddington, G., J. Am. Chem. Soc., 1954, 76, 4791

McCullough, J.P., Pennington, R.E., Waddington, G., J. Am. Chem. Soc., 1952, 74, 4439

McGlashan, M.L., Potter, D.J.B., Proc. Roy. Soc., 1962, A267, 478

Michels, A., Michels, C., Wouters, H., Proc. Roy. Soc., 1935, A153, 214

Michels, A., Wassenaar, T., Zwietering, T.N., Physica, 1952, 18, 67

Moreland, M.R., McKetta, J.J., Silberberg, I.H., J. Chem. Eng. Data, 1967, 12, 329

Najour, G.C., King, A.D., J. Chem. Phys., 1966, 45, 1915

Opel, G., Schaffenger, J., Wiss. Z. Univ. Rostock, Math-Naturwiss, 1969, 18, 871

Patee, E.C., Brown, G.G., Ind. Eng. Chem., 1934, 26, 511

Perry, J.H. (Ed.,), Chemical Engineer's Handbook, 4th Ed., Tokyo, Kogakusha

Roper, A.E., J. Phys. Chem., 1940, 44, 835

Sage, B.H., Kennedy, E.R., Lacey, W.N., Ind. Eng. Chem., 1936, 28, 601

Schamp, H.W., Mason, E.A., Richardson, A.C.B., Altman, A., Phys. Fluids, 1958, 1, 329

Scott, R.L., Dunlap, R.D., J. Phys. Chem., 1962, 66, 639

Slawsky, Z.I., Seigel, A.E., Ho, L.T., Kopp, H.J., Van der Slice, J.T., Rev. Sci. Instr., 1959, 30, 679

Solbrig, C.H., Ellington, R.T., Chem. Eng. Prog. Sym. Seri., 1963, 59 No. 44, 127

Straty, G.C., Prydz, R., Rev. Sci. Instr., 1970, 41, 1223

Stockett, A.L., Wenzel, L.A., A.I.Ch.E.J., 1964, 10, 557

Thomaes, G., van Steenwinkel, R., Rev. Sci. Instr., 1960, 31, 825

Topping, J., Errors of Observation and their Measurement, London, Institute of Physics, 1955

Ulmer, G., Research Techniques at High Pressure and High Temperature, Berlin, Springer and Verlag, 1971

Varekamp, F.H., Beenakker, J.J.M., Physica, 1959, 25, 889

Vigdergauz, M., Semkin, V., J. Chromatgr., 1971, 58, 95

Waddington, G., Todd, S.S., Huffman, J.M., J. Am. Chem. Soc., 1947, 69 22

Wallace, C.B., Silberberg, I.H., McKetta, J.J., Hydro. Proc., 1964, 43, 177

Walters, C.J., Smith, J.M., Chem. Eng. Prog., 1952, 48, 337

Weast, R.C. (Ed.), Handbook of Chemistry and Physics, 49th Ed., Cleveland, The Chemical Rubber Co., 1968

White, D., Rubin, T., Camky, P., Johnston, H.L., J. Phys. Chem., 1960, 64, 1607

White, D., Hu, J-H., Johnston, H., J. Chem. Phys., 1953, 21, 1149

Whytlaw-Gray, R., Bottomley, G.A., Nature, 1957, 180, 1252

Williamson, A.G., Ann. Rev. Phys. Chem., 1964, 15, 63

FIGURE 9.1

LEAST SQUARES STRAIGHT LINE

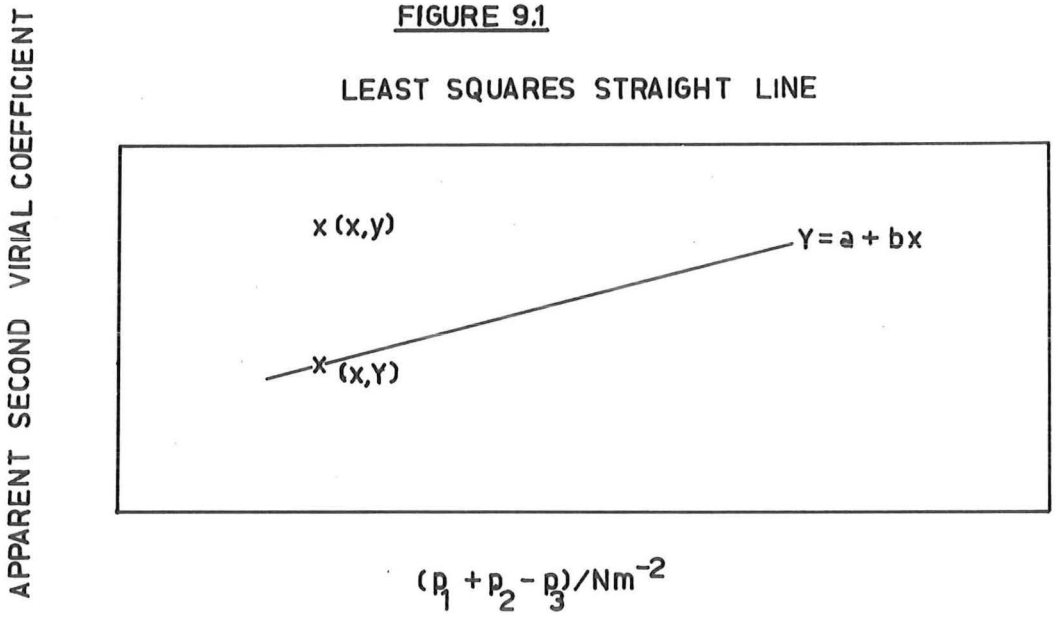
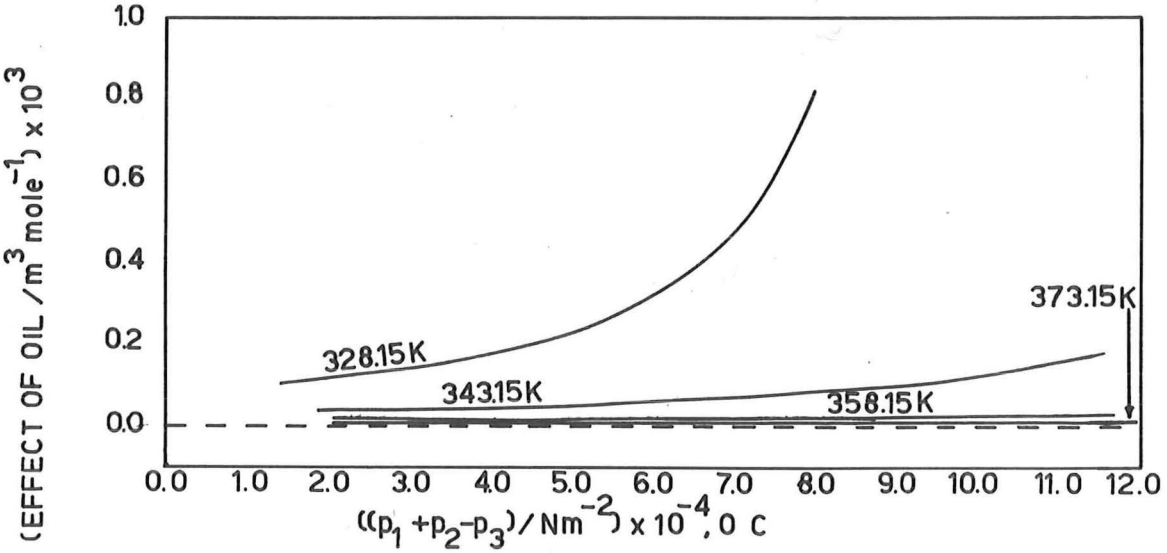


FIGURE 9.2

EFFECT OF OIL ON THE SECOND VIRIAL COEFFICIENT



9. APPENDIX

9.1 Weighted Least Squares Straight Line

In figure 9.1, $(p_1 + p_2 - p_3)$ is plotted along the x-axis while $B'_{apparent}$ is plotted on the y-axis. The points (x,y) are the experimental points while the line, Y = a+bx, through the points (x,Y) is the least squares fit.

Davies (1967) shows that the sum of squares of the deviations from the line Y = a+bx, Q, is given by:

$$Q = \sum_{i=1}^{n} (y_i - (a + bx_i))^2 \qquad (9.1)$$

where a and b are the regression coefficients. These coefficients are chosen so that Q is a minimum. Hence:

$$\frac{\partial Q}{\partial a} = \Sigma (y_i - (bx_i + a))(-2) = 0 \qquad (9.2)$$

$$\frac{\partial Q}{\partial b} = \Sigma (y_i - (bx_i + a))(-2x_i) = 0 \qquad (9.3)$$

Since the accuracy of the values of the apparent second virial coefficient, $B'_{apparent}$, is a function of the pressure term $(p_1 + p_2 - p_3)$ at a given temperature, the least squares analysis requires weighting. This can be achieved by applying a factor z to the deviation $(y_i - (a+bx_i))$ where z bears a relation to $(p_1 + p_2 - p_3)$. The equations describing the regression coefficients become:

$$\frac{\partial Q}{\partial b} = \sum_{i=1}^{n} z(y_i - (bx_i+a))(-2x_i) = 0 \qquad (9.4)$$

$$\frac{\partial Q}{\partial a} = \sum_{i=1}^{n} z(y_i - (bx_i+a))(-2) = 0 \qquad (9.5)$$

It can be shown that for the weighted sums of the squares of the deviations to be a minimum the regression coefficients are given by:

$$a = \frac{\Sigma yz - \Sigma bzx}{\Sigma z} \qquad (9.6)$$

$$b = \frac{\Sigma z \Sigma xyz - \Sigma xz \Sigma yz}{\Sigma x^2 z \Sigma z - (\Sigma xz)^2} \qquad (9.7)$$

The probable error, as given in section 4.3, can be determined by the following equation:

$$\delta B' = \sqrt{\left(\frac{6RT\delta p}{p^2}\right)^2 + \left(\frac{4\delta TR}{p}\right)^2} + \left(\frac{RT}{p}\right)^2 \frac{2\delta n}{V} + \frac{4B'\delta p}{p} + \frac{2B'RT\delta n}{pV} \qquad (9.8)$$

where δT is 0.02 K, δn is 1×10^{-6} moles, δp = 3.71 N m^{-2},

and p is p_2 the maximum pressure at each loading.

A graph of $\ln\delta B'$ versus $\ln(p_1+p_2-p_3)$ at a given temperature produces a straight line so that

$$\ln\delta B' = g\ln x + d \qquad (9.9)$$

where both g and d are constants and $x = (p_1+p_2-p_3)$.

Hence

$$\frac{1}{\delta B'} = fx^{-g} \qquad (9.10)$$

where f is another constant.

The term $\frac{1}{\delta B'}$ would be an appropriate weighting factor for the least squares analysis.

$$z = \frac{1}{\delta B'} = fx^{-g} \qquad (9.11)$$

in which both f and g are functions of temperature since the uncertainty in the second virial coefficient is dependent on both temperature and pressure.

On substitution into equations 9.6 and 9.7, the regression coefficients become:

$$b = \frac{\Sigma x^{-g}\Sigma x^{1-g}y - \Sigma x^{1-g}\Sigma yx^{-g}}{\Sigma x^{2-g}\Sigma x^{-g} - (\Sigma x^{1-g})^2} \qquad (9.12)$$

$$a = \frac{\Sigma yx^{-g} - b\Sigma x^{1-g}}{\Sigma x^{-g}} \qquad (9.13)$$

A table of $\delta B'$ at values of $(p_1 + p_2 - p_3)$ for 20 K intervals in temperature from 313.15 K to 393.15 K was drawn up. With the use of a Hewlett-Packard least squares power curve fitting program the points ($\delta B'$,x) were curve fitted at each temperature to produce a relationship of the form:

$$\delta B' = ax^b \qquad (9.14)$$

Different values for the constants a and b were obtained at each temperature and these values were fitted to a curve of the form

$$a \text{ or } b = mT + c \tag{9.15}$$

where both m and c were constants.

The resulting equations were:

$$a = 4.30\times10^{2}\ T - 1.026\times10^{5} \tag{9.16}$$

$$b = -5.34\times10^{-4}\ T - 1.68 \tag{9.17}$$

Hence the equation describing the probable error in B' as a function of T and $(p_1 + p_2 - p_3)$ can be written as:

$$B' = (4.30\times10^{2}\ T - 1.026\times10^{5})(p_1+p_2-p_3)^{(-5.34\times10^{-4}\ T-1.68)} \tag{9.18}$$

The value of g in the weighted regression coefficient, expressions 9.12 and 9.13, is given by

$$g = -5.34\times10^{-4}\ T - 1.68 \tag{9.19}$$

A value for the accuracy of regression coefficients is given by the standard error from Topping (1955).

$$\text{Standard error at b} = \sqrt{\frac{n\Sigma(y-Y)^2}{(n-2)(n\Sigma x^2-(\Sigma x)^2)}} \tag{9.20}$$

$$\text{Standard error at a} = \sqrt{\frac{\Sigma(y-Y)^2\Sigma x^2}{(n-2)(n\Sigma x^2-(\Sigma x)^2)}} \tag{9.21}$$

The standard errors of the regression coefficients are weighted in a similar manner to the least squares fit of the second virial coefficient values with the maximum pressure reading having a weight of one. The term (y-Y) in the equations for the standard errors of the regression coefficients 9.20 and 9.21 is multiplied by the factor $(p/p_{max})^{\alpha}$ where p_{max} is the maximum pressure reading from the manometer at the given temperature for all of the points and p is the corresponding pressure for the point under consideration. Hence the standard errors of the regression coefficients are given by:

$$\text{standard error of b} = \sqrt{\frac{n\Sigma((y-Y)(p/p_{max})^{\alpha})^2}{(n-2)(n\Sigma x^2 - (\Sigma x)^2)}} \qquad (9.22)$$

$$\text{standard error of a} = \sqrt{\frac{\Sigma((y-Y)(p/p_{max})^{\alpha})^2 \Sigma x^2}{(n-2)(n\Sigma x^2 - (\Sigma x)^2)}} \qquad (9.23)$$

where α is given by:

$$\alpha = 1.68 + 5.34 \times 10^{-4} T \qquad (9.24)$$

9.2 Effect of Oil within One Cell of the Apparatus

If it is assumed that there is a trace of oil in one of the cells of the apparatus, say cell I, and Raoult's Law is applied, then:

$$p = p^o x \qquad (9.25)$$

where p is the partial pressure of n-hexane over an oil-n-hexane mixture with a mole fraction of x where x is given by

$$x = \frac{\delta}{b + \delta} \qquad (9.26)$$

and δ is the number of moles of n-hexane in the oil and b is the number of moles of oil.

Hence the number of moles of n-hexane removed from the bulk gas because of that dissolved in the oil is given by

$$\delta = \frac{pb}{p^o - p} \qquad (9.27)$$

With the oil in cell I alone the pressure series virial equations for the three pressure measurements become:

$$p_1(V_1 + \Delta V) = (n-\delta_1)RT + (n-\delta_1)B'p_1 + (n-\delta_1)C'p_1^2 \qquad (9.28)$$

$$p_2(V_2 + \Delta V) = nRT + nB'p_2 + nC'p_2^2 \qquad (9.29)$$

$$p_3(V_1+V_2+\Delta V) = (n-\delta_3)RT + (n-\delta_3)B'p_3 + (n-\delta_3)C'p_3^2 \qquad (9.30)$$

By eliminating V_1 and V_2 from these equations, it can be shown that:

$$B'+C'(p_1+p_2-p_3) = B'_{apparent} + \frac{B'}{n}(\delta_1-\delta_3) + \frac{RT}{n}\left(\frac{\delta_1}{p_1}-\frac{\delta_3}{p_3}\right) + \frac{C'}{n}(p_1\delta_1-p_3\delta_3) \tag{9.31}$$

but the term $\frac{C'}{n}(p_1\delta_1 - p_3\delta_3)$ is small so that this equation becomes

$$B'+C'(p_1+p_2-p_3) = B'_{apparent} + \frac{B'}{n}(\delta_1-\delta_3) + \frac{RT}{n}\left(\frac{\delta_1}{p_1} - \frac{\delta_3}{p_3}\right) \tag{9.32}$$

Since $p_3 \simeq \frac{1}{2}p_1$, $p_1V_1 \simeq nRT$ and $\delta = \frac{pb}{p^o-p}$

$$B'+C'(p_1+p_2-p_3) = B'_{apparent} + \frac{B'bRT}{V_1}\left(\frac{1}{p^o-p_1} - \frac{1}{2(p^o-\frac{1}{2}p_1)}\right)$$

$$+ \frac{(RT)^2b}{p_1V_1}\left(\frac{1}{p_o-p_1} - \frac{1}{(p^o-\frac{1}{2}p_1)}\right) \tag{9.33}$$

In the original analysis the right-hand side of equation 9.33, without the oil terms, is plotted against $(p_1 + p_2 - p_3)$ to obtain a value of B'. The extra oil terms have a considerable effect, especially at low temperatures, as shown in figure 9.2 where the straight dashed line is an assumed no oil plot of $B'_{apparent}$. The curves, one at each of the four temperatures used in this work, are those obtained using the following values: at each temperature the value of B' used is that taken from the literature plot in figure 6.5, $b = 1.4\times10^{-4}$ moles, $V_1 = 1.5\times10^{-3}$ m^3 and p^o (initially calculated in mmHg) was obtained using the equation below (Weast, 1968).

$$\log_{10} p^o = \frac{1654.6}{T} + 7.724 \tag{9.34}$$

The results obtained by recalculating a value of B' assuming this amount of oil are shown in table 9.1 and plotted in figure 7.1.

Table 9.1

T/K	$(B'/m^3\ mole^{-1}) \times 10^5$	$(C'/m^5\ mole^{-1}\ N^{-1}) \times 10^{11}$
328.15	-155	457
343.15	-135	48
358.15	-122	27
373.15	-112	54